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ON THE ACTION OF BENZIMIDOMETHYL ETHER ON AROMATIC ORTHO COMPOUNDS.

BY H. L. WHEELER.

This paper consists of a description of benzimidomethyl ether and of its action on orthoamidophenol, orthoamidothiophenol, orthophenylenediamine, and on orthotoluylenediamine. These reactions resulted in the formation of anhydrobases.

Benzimidomethyl Ether.—Tafel and Enoch[1] have shown that by the action of ethyl iodide on the silver salt of benzamide, benzimidoethyl ether is formed. The benzimidomethyl ether used in these experiments was prepared in the same manner. Silver benzamide, suspended in dry ether, was treated with an excess of methyl iodide, and, after standing several days, the mixture was diluted with more ether. It was then filtered and, on evaporating off the ether on the water-bath, the benzimidomethyl ether was obtained as a light yellow colored oil. This, on cooling to $-30°$, did not solidify. It has a peculiar, but not unpleasant, aromatic odor. It dissolves in acids and is precipitated again by alkali or ammonia. The hydrochloric acid solution gives yellow crystalline precipitates with both gold and platinum chlorides. For analysis the

[1] Ber. d. chem. Ges., **23**, 104.

platinum-chloride precipitate was washed with dilute hydrochloric acid and dried over sulphuric acid.

0.1960 gram substance gave 0.0570 gram platinum.

	Found.	Calculated for $[C_6H_5.CCl(NH_2)OCH_3]_2.PtCl_4$.
Pt = 195.5	29.0	28.7

For purposes of comparison benzimidomethyl ether was prepared by the action of hydrochloric acid gas on a mixture of benzonitrile and methyl alcohol, according to the method of Pinner.[1] From the hydrochloric-acid addition-product thus obtained, the free imido-ether was liberated by means of potassium carbonate. This was found to have properties identical with the above.

Benzimidomethyl ether differs from benzimidoethyl ether, its homologue, by not readily yielding cyanphenine on standing. Indeed, Pinner[2] states that the best method for preparing cyanphenine is to allow benzimidoethyl ether to stand.

Benzimidomethyl ether was allowed to stand exposed to the air in a beaker glass for several weeks. Colorless crystals were slowly formed. These were washed from unaltered benzimidomethyl ether with ligroïn and then crystallized from dry benzene. The product then melted below 60°. On recrystallizing from benzene it melted from 120°–125°; again recrystallized, it melted at 128°. It was readily soluble in alcohol and in ether, and crystallized from water in plates. The substance was, therefore, benzamide. It was further identified as benzamide by preparing the silver salt.

In another experiment a few drops of the imido-ether were covered with a layer of water, in which it is somewhat soluble, and the whole allowed to stand. In about a month the oil had completely changed into well-crystallized plates of benzamide. The formation of benzamide by the action of water on benzimidomethyl ether seems to be best explained by the assumption that, first, an addition of water takes place, and that the resulting compound then gives off methyl alcohol as follows:

$$C_6H_5.C(NH_2)\begin{matrix}O\\ \diagdown\\ \diagup\\ OCH_3\end{matrix}\!\!\begin{matrix}H\\ \\ \\ \end{matrix} = C_6H_5.CO.NH_2 + CH_3OH.$$

[1] Ber. d. chem. Ges., **16**, 354. 1654.
[2] Ber. d. chem. Ges., **22**, 1611.

Benzenylorthoamidophenol, $C_6H_5.C\overset{N}{\underset{O}{<}}C_6H_4$.—The investigation of the action of benzimidomethyl ether on orthoamidophenol was undertaken in order to determine whether an oxyamidine would result, *i. e.*, $C_6H_5.C\overset{NH}{\underset{NH.C_6H_4OH}{<}}$. This then, by dehydration, might lead to a phenanthridine synthesis. However, no evidence was found of the formation of such a compound. The only crystalline product obtained was benzenylorthoamidophenol, the condensation taking place according to the following:

$$C_6H_5.C\overset{NH\quad H_2}{\underset{OCH_3\quad H}{<}}\overset{N}{\underset{O}{>}}C_6H_4=C_{13}H_9NO+CH_3OH+NH_3.$$

This reaction is, therefore, similar to that observed by Sandmeyer[1] in the case of imidocarbonic ethyl ether and aromatic ortho compounds.

When orthoamidophenol and benzimidomethyl ether are mixed and warmed on the water-bath (the reaction takes place slowly, if at all, in the cold) ammonia and methyl alcohol are given off. The reaction requires only a few minutes for its completion. On cooling, the mass solidifies. Any unaltered amidophenol can be removed by shaking the ethereal solution with alkali; nothing but amidophenol was obtained from the alkaline solution. On evaporating off the ether and crystallizing the residue from dilute alcohol, the anhydro-base separates in beautiful long yellow needles. It can be obtained colorless by distilling in a current of steam, or by dissolving it in concentrated hydrochloric or sulphuric acid and diluting with water. It then separates in the form of shining plates melting at 103°. These separate from dilute alcohol in long needles. A nitrogen determination gave the following results:

0.4064 gram of substance gave 25.5 cc. N at 17.5° and 751 mm.

	Found.	Calculated for $C_6H_5C\overset{N}{\underset{O}{<}}C_6H_4$.
N	7.18	7.18

[1] Ber. d. chem. Ges., **19**, 2650.

No salts of this base were obtained except the platinum and gold double salts. The latter can be crystallized from alcohol containing concentrated hydrochloric acid. It then separates in the form of shining yellow needles. These are immediately decomposed by cold water. Analysis:

0.1960 gram substance gave 0.0719 gram Au.

	Found.	Calculated for $C_6H_5C\langle\overset{N}{O}\rangle C_6H_4.HCl.AuCl_3$.
Au = 197.2	36.7	36.8

This base is, therefore, benzenylorthoamidophenol. Ladenburg[1] has shown that this compound was probably first obtained by Morse by the action of benzoyl chloride or orthoamidophenol hydrochloride. Ladenburg obtained it by acting on the free amidophenol with benzoyl chloride. On distilling, the fraction boiling between 314°–317° was found to contain this compound. This temperature is erroneously given in the text-books as its boiling-point. An experiment with the pure compound, using an Anschütz thermometer, showed that the compound boiled above 360°. This compound was also obtained by Hübner and Stünkel[2] from orthonitrophenyl benzoate.

Benzenylorthoamidophenol can also be obtained by distilling orthoamidophenol with benzamide. Benzamide reacts in this case, therefore, as if it had the structure $C_6H_5.C(OH):NH$ analogous to the imido ether. It seems more probable though that the reaction takes place, first, with the formation of amidophenyl benzoate, since Guareschi[3] has shown that benzamide reacts with phenol forming phenol benzoate, and the amidophenol benzoate thus formed, then—as Hübner and Stünkel[4] have shown—readily loses water with the formation of the anhydro-base.

It can also be obtained by distilling orthoamidophenol with benzonitrile, by boiling with benzaldehyde, or by heating mixtures of the amidophenol and benzanilide in a sealed tube to 250° and then distilling. The crude products thus obtained dissolve in ether with a greenish-yellow fluorescence and crystallize from alcohol in yellow needles.

[1] Ber. d. chem. Ges. **9**, 1526. [2] Ann. Chem. (Liebig), **208**, 290.
[3] Ann. Chem. (Liebig), **171**, 140. [4] *Loc. cit.*

Benzenylorthoamidothiophenol, $C_6H_5.C\begin{matrix}/\!/ N \\ \backslash S\end{matrix}\rangle C_6H_4$.—The thiophenol necessary for this experiment was prepared from the disulphide $\begin{matrix}S.C_6H_4.NH_2 \\ | \\ S.C_6H_4.NH_2\end{matrix}$ by reduction with tin and hydrochloric acid, according to the directions of Hofmann.[1]

2.4 grams orthoamidothiophenol and 2.6 grams benzimidomethyl ether were mixed in ethereal solution and evaporated to dryness on the water-bath without any apparent reaction taking place. On heating to 110°, ammonia and methyl alcohol were given off. When the evolution of ammonia had practically ceased, the mass was cooled. It was then dissolved in concentrated hydrochloric acid and filtered from a trace of insoluble matter. The anhydro-base was precipitated by adding water. It separated as a curdy, white mass which, by the following properties, was readily identified as benzenylorthoamidothiophenol (benzenylamidophenylmercaptan), described by Hofmann.[2] It melts at 114°–115°. On crystallizing from dilute alcohol or hydrochloric acid, it separates in long, colorless needles having the odor of roses and geraniums.

Benzenylorthophenylenediamine, $C_6H_5.C\begin{matrix}/\!/ N \\ \backslash NH\end{matrix}\rangle C_6H_4$.—Benzimidomethyl ether reacts with orthodiamines, phenylenediamine for example, according to the following:

$$C_6H_5C\begin{matrix}/\!/ \boxed{NH_2}\ N \\ \backslash \boxed{OCH_3}\ HN\end{matrix}\rangle C_6H_4 = C_{13}H_{10}N_2 + CH_3OH + NH_3.$$

1.8 grams of benzimidomethyl ether and 1.2 grams of orthophenylenediamine were mixed in ethereal solution and evaporated to dryness on the water-bath. At first there was no evidence of a reaction, but on heating for a few minutes on the water-bath the reaction slowly took place. It may be hastened by warming to 115°–120°, but then a slight decomposition of the imido ether takes place. In a short time the mass began to solidify. After the reaction was ended the product was washed with chloroform; this left the anhydrobase in the form of colorless tables which, by their high melt-

[1] Ber. d. chem. Ges., **12**, 2363. [2] *Loc. cit.*

ing-point, *i. e.*, 280°, were readily identified as benzenylorthophenylenediamine or anhydrobenzdiamidobenzene, which Hübner[1] obtained by reducing orthonitrobenzanilide. The following properties also served to identify it. The base is difficultly soluble in benzene and chloroform, also in water. It is somewhat soluble in sodium hydroxide but not in ammonia, which readily precipitates its acid solutions. It yields a difficultly soluble nitrate and sulphate. The hydrochloric acid salt was easily soluble in warm water but quite difficultly soluble in hydrochloric acid. The hydrochloric-acid solution of the base gives a yellow precipitate with gold chloride. This, on crystallizing from alcohol diluted with hydrochloric acid, separates in the form of fine long yellow needles. The crystals are readily soluble in alcohol but very difficultly soluble in water and hydrochloric acid. Analysis:

0.1375 gram substance gave 0.0503 gram Au.

	Found.	Calculated for $C_6H_5C\langle\overset{N}{NH}\rangle C_6H_4.HCl.AuCl_3$.
Au = 197.2	36.5	36.8

Benzenylorthotoluylenediamine, $C_6H_5C\langle\overset{N}{NH}\rangle C_6H_3.CH_3$.—Two grams of orthotoluylenediamine (CH_3,NH_2,NH_2,:1,3,4.) were mixed with 2 grams of benzimidomethyl ether and heated on the water-bath. Methyl alcohol and ammonia were given off and the mass soon solidified. The product was then crystallized from dilute alcohol. It separated as a yellowish white crystalline mass melting from 238°–240°. It was found to be identical with the compound obtained by Hübner[2] by the action of benzoyl chloride on benzmetamidoparatoluidine. It can be readily purified by converting it into the sulphate or hydrochloride which, as Hübner observed, are difficultly soluble in water. On adding gold chloride to the hot hydrochloric-acid solution of the base, a gold double salt is formed. This separates, on cooling, in the form of beautiful long yellow needles. These, dried over sulphuric acid, gave the following result on analysis:

0.1845 gram substance gave 0.0661 gram Au.

[1] Ann. Chem. (Liebig), **208**, 302.
[2] Ann. Chem. (Liebig), **208**, 316.

	Found.	Calculated for $C_8H_3C\langle{}^{N}_{NH}\rangle C_8H_3.CH_3.HCl.AuCl_3$.
Au = 197.2	35.8	35.9

Experiments were undertaken in order to obtain an anhydro-base from orthiobromaniline and benzimidomethyl ether, without success.

ON THE ACTION OF SOME INORGANIC CYANIDES UPON CHLOROCAFFEINE.[1]

By M. Gomberg.

Caffeinecarboxylamide.

In a previous paper[2] upon *Trimethylxanthine and Some of its Derivatives*, I have briefly described a compound obtained by the action of potassium cyanide upon chlorocaffeine. The insoluble product thus obtained did not agree with the formula of cyanocaffeine, the preparation of which was the object of the experiment. According to E. Fischer,[3] prolonged boiling of bromocaffeine with a dilute alcoholic solution of potassium cyanide results in the formation of a small quantity of *amidocaffeine*. It was reasonable to suppose that the action of potassium cyanide upon chlorocaffeine would be similar to that upon the bromo-compound. But whenever chlorocaffeine was boiled under an inverted condenser with the calculated quantity of potassium cyanide in 70–80-per cent. alcohol, there always came down within one to two hours a precipitate consisting of a heavy, amorphous, slightly yellowish powder. This was filtered off, washed with hot alcohol, water, dilute hydrochloric acid, and dried at 110° C. The yield was usually from 80–85 per cent. of the weight of chlorocaffeine employed. The compound is insoluble in either hot or cold water, alcohol, chloroform, ether, or benzene; soluble in strong mineral acids. It does not melt at 360° C. The results of elementary analysis showed this compound to be neither cyanocaffeine nor amidocaffeine, as will be seen on comparing the theoretical figures with those obtained as an average of a great many determinations.

[1] From the author's thesis, presented for the degree of Doctor of Science to the Council of the Graduate School of the University of Michigan, June, 1894.

[2] This Journal, **14**, 611.

[3] Ann. Chem. (Liebig), **215**, 266.

	Calculated for $C_8H_9(CN)N_4O_2$.	Calculated for $C_8H_9(NH_2)N_4O_2$.	Found.
C	49.31	33.50	45.70
H	4.12	5.30	4.83
N	31.96	33.50	29.56

The subject has since been studied more in detail, and the results of the investigation are presented in the following paper.

Action of Potassium Cyanide upon Bromocaffeine.—10 grams of bromocaffeine were boiled together with 3 grams of potassium cyanide in 300 cc. of 80-per cent. alcohol. Within less than two hours a heavy, amorphous precipitate separated; this was filtered off, washed with hot alcohol, dilute hydrochloric acid, and water, and finally dried at 110° C. The yield was 8 grams. In appearance and in solubility, this compound seemed to be identical with that obtained from chlorocaffeine, and this is confirmed by the elementary analysis:

I. 0.2154 gram gave 0.3627 gram CO_2 + 0.0935 gram H_2O.
II. 0.1644 gram gave 0.2736 gram CO_2 + 0.0720 gram H_2O.
III. 0.1758 gram gave 44 cc. N at 14° and 754 mm.
IV. 0.2280 gram gave 59.3 cc. N at 16° and 734 mm.
V. 0.1755 gram gave 44.2 cc. N at 14° and 742 mm.

Calculated in percentage the results are:

	I.	II.	III.	IV.	V.	Mean.
C	45.91	45.43	....	....	....	45.67
H	4.83	4.86	....	....	....	4.85
N	....	....	29.68	29.83	29.39	29.63

It was suggested in the previous paper that the compound described above might be caffeine, in which the hydrogen of the (CH) group is replaced by the ($CONH_2$) group. In other words, cyanocaffeine *is* produced in the reaction, but is only an intermediate product; and it suffers partial saponification as soon as formed, with the production of *caffeinecarboxylamide*.

$$C_6(CH_3)_3ClN_4O_2 + KCN = C_6(CH_3)_3(CN)N_4O_2 + KCl.$$
$$C_6(CH_3)_3(CN)N_4O_2 + H_2O = C_6(CH_3)_3(CONH_2)N_4O_2.$$

The supposition that we had here an acid-amide was based,

primarily, upon the results of the ultimate analysis, as is seen on comparing them with the theoretical figures:

	Calculated for $C_8H_9(CONH_2)N_4O_2$.	Found.
C	45.56	45.70
H	4.56	4.83
N	29.54	29.56

The second reason for assuming that we had here a partially saponified nitrile, was the probability of the reaction. The direct formation of an acid-amide from a halogen compound, through the action of potassium cyanide, is somewhat rare, but not altogether unusual. The view expressed above has since been entirely substantiated (1) by withdrawing the elements of water from caffeinecarboxylamide, and thus obtaining cyanocaffeine; (2) by estimating the amount of carbon dioxide produced when the acid-amide is heated with sulphuric acid, and (3) by the further saponification of the acid-amide to caffeinecarboxylic acid.

Cyanocaffeine.

Action of Phosphorus Pentoxide.—Five grams of caffeinecarboxylamide, thoroughly mixed with about an equal quantity of phosphorus pentoxide, were heated in an oil-bath at 250° C., for several hours. The mixture turned very dark and a considerable amount of tarry material was formed. The mass, on cooling, was extracted with alcohol, and the latter, when cold, gave a dark granular deposit. This was now dissolved in chloroform, and to the filtered chloroform solution ether was gradually added till the solution became turbid. In a short time there appeared a crystalline deposit, separating in small beautiful rosettes of yellow color. The yield was rather small—about 1.5 grams. The compound, dried at a gentle heat to a constant weight, was analyzed with the following results:

I. 0.1720 gram gave 0.3082 gram CO_2 + 0.0641 gram H_2O.

II. 0.1825 gram gave 52.8 cc. N at 20° and 730 mm.

Another sample, prepared more carefully and having only a slight yellow tint, furnished these figures:

III. 0.2912 gram gave 0.5262 gram CO_2 + 0.1099 gram H_2O.

IV. 0.2408 gram gave 69.6 cc. N at 28° and 743 mm.

	Calculated for $C_5H_3(CN)H_4O_3$.	Found I.	II.	III.	IV.
C	49.31	48.87	....	49.34	....
H	4.12	4.13	....	4.19	....
N	31.96	....	32.52	....	32.19

The effect of the phosphorus pentoxide is, of course, the removal of one molecule of water from a molecule of caffeinecarboxylamide,

$$C_5H_3(CONH_2)N_4O_2 - H_2O = C_5H_3(CN)N_4O_2.$$

It was found by repeated experiments that it is not necessary to heat the mixture above 180°–200° C. Moreover, if the fusion is allowed to go on quietly, without any stirring, for about twenty minutes before completing the experiment, the mixture will separate into two layers: an upper spongy, dark layer of phosphoric acid, and a pale-yellow, compact mass of cyanocaffeine at the bottom of the tube. The cyanocaffeine can thus, at once, be separated from the phosphoric acid mechanically in very pure condition.

Cyanocaffeine can be obtained perfectly white by repeatedly dissolving it in chloroform and precipitating with ether; also by recrystallization from hot alcohol. When obtained by either of the above processes, or by sublimation, it consists of small prismatic crystals, belonging, probably, to the triclinic system, and peculiarly arranged in clusters. It melts at 151° C., and does not congeal till the temperature sinks to 109°–110°. It sublimes without decomposition at about 160°. The compound is soluble in hot water, hot alcohol, dilute or strong; soluble in methyl alcohol, very soluble in chloroform, more soluble in hot benzene than in cold, insoluble in ether.

The behavior of cyanocaffeine towards water and dilute alcohol is worthy of notice. In the action of potassium cyanide upon chlorocaffeine in dilute alcohol, the formation of caffeinecarboxylamide was explained by the assumed instability of the cyano-compound and its great tendency towards assimilation of water. When, however, cyanocaffeine, prepared by dehydration of the acid-amide, is dissolved in boiling water, or in boiling dilute (50–70-per cent.) alcohol, it does not show any such great tendency towards hydration. When boiled with water, it changes into the insoluble acid-

amide, but not until after about thirty to sixty minutes' boiling, while with dilute alcohol the cyanocaffeine can be boiled for over an hour without any saponification into the acid-amide. But when to the hot solution of the cyano-compound in either water or dilute alcohol, a fragment of potassium cyanide is added, there appears, within two to three minutes, a precipitate of the insoluble acid-amide. The change is rapid and complete. The chlorides of potassium and sodium do not seem to bring about the hydration in the same manner as the potassium cyanide does. Nor has the latter the same effect at all when methyl alcohol is substituted for ethyl alcohol. When strong ethyl alcohol (97–98-per cent.) is used as a solvent for cyanocaffeine, the solution can be boiled for hours, with or without the addition of potassium cyanide, and no hydration takes place. The same is true of methyl alcohol, even when only 75–80-per cent. strong.

This influence of potassium cyanide upon cyanocaffeine offers a satisfactory explanation, why caffeinecarboxylamide and not cyanocaffeine is formed, when chlorocaffeine is acted upon by a solution of potassium cyanide in dilute alcohol.

The preparation of cyanocaffeine by a direct method was then undertaken by using different cyanides and varying the nature of the solvents.

Action of Potassium Cyanide upon Chlorocaffeine in Absolute Alcohol.—Henry[1] has called attention to the fact that the interchange of the cyanogen group for the halogen atom takes place usually when the alcohol is dilute. This would be especially true when the operation is conducted at ordinary atmospheric pressure, since potassium cyanide is almost insoluble in absolute alcohol. In this instance, there was no action whatever when chlorocaffeine and potassium cyanide in absolute alcohol were boiled under an inverted condenser for several days. Chlorocaffeine was next mixed with a little more than the calculated quantity of potassium cyanide in absolute alcohol, and the sealed tube heated at 100° for fifteen hours. The alcohol was then driven off on the water-bath and the residue digested with chloroform, in which both chlorocaffeine and cyanocaffeine are easily soluble. To the fil-

[1] Compt. rend., **104**, 1181.

tered chloroform solution ether was gradually added. The white precipitate which came down at this stage was entirely unlike the definitely crystalline form of cyanocaffeine. It melted sharp at 187°, the melting-point of chlorocaffeine being 188°. In appearance and behavior, as well as in the percentage of chlorine it contained, the substance was identified as pure unchanged chlorocaffeine.

Samples were then heated at 150°–160° for about five hours. The resulting product was of a dark greenish color, extremely difficult of purification. It was found to consist, for the most part, of unchanged chlorocaffeine, some caffeinecarboxylamide, and, perhaps, a small quantity of cyanocaffeine. The only indication that the latter was present, was furnished by a small crop of crystals obtained by fractional precipitation, which melted considerably lower than chlorocaffeine and a little higher than cyanocaffeine.

Action of Potassium Cyanide in Water.—When chlorocaffeine was heated with the calculated quantity of potassium cyanide, or with an excess of it, in water, there was apparently no reaction to speak of, even when the boiling was continued for three days. The large, bulky mass which separated on cooling was found to contain a small quantity of caffeinecarboxylamide, the rest being pure unchanged chlorocaffeine, as was shown by the melting-point and the percentage of chlorine.

Action of Potassium Cyanide in Methyl Alcohol.—Potassium cyanide appears to be more soluble in methyl alcohol, both dilute and strong, than in ethyl alcohol. Calculated quantities of chlorocaffeine and potassium cyanide in about 90-per cent. methyl alcohol, were boiled under an inverted condenser for several hours. The residue, after evaporation of the alcohol, was considerably colored, the green color usually increasing in depth with the dilution of the alcohol and the length of boiling. The mixture was treated and examined, as described under ethyl alcohol, and showed, beyond any doubt, the presence of some cyanocaffeine. The melting-point varied in different samples from 145°–160°, but ultimate analysis showed that in no case did the amount of cyanocaffeine exceed 20 per cent., the rest being chlorocaffeine. All efforts to sepa-

rate these two compounds were unsuccessful, since chlorocaffeine and cyanocaffeine resemble each other so closely in their solubility in water, alcohol, chloroform, etc. Diluting the alcohol to 50–70 per cent. did not give any better yield. In all instances the formation of the acid-amide was only very slight or none at all.

When absolute methyl alcohol was substituted for the dilute alcohol, the results were practically the same, the products being purer. Samples were then heated with absolute alcohol in sealed tubes at 100°. The contents became highly colored, even at the end of two hours. They were found to contain large quantities of unchanged chlorocaffeine, some caffeinecarboxylamide, and a small quantity of the cyanocompound.

Action of Mercuric Cyanide.—Heating chlorocaffeine with mercuric cyanide in alcohol for several days, under an inverted condenser, gave no indication of the formation of either cyanocaffeine or the acid-amide. When the heating was conducted under pressure, at 150°–200° for twenty hours, a small quantity of the acid-amide was formed, and a little separation of metallic mercury took place; otherwise the chlorocaffeine remained white and unchanged.

Action of Potassium Mercuric Cyanide.—It was very surprising to find that the double salt had no action upon chlorocaffeine. The experiments were made by using both dilute and strong ethyl alcohol,[1] methyl alcohol, and water. The heating was conducted under inverted condensers and in sealed tubes, at temperatures varying from 100°–200°, but beyond the separation of some metallic mercury and the formation of a small quantity of the acid-amide, the analysis showed that the chlorocaffeine was not attacked.

Action of Potassium Cyanide upon Fused Chlorocaffeine.—Chlorocaffeine was thoroughly mixed with finely powdered potassium cyanide, placed in a test-tube and heated in a sulphuric-acid bath, the temperature being determined by a thermometer in the tube. At about 200° the chlorocaffeine was all melted. The mixture was kept at that temperature for

[1] The double salt potassium mercuric cyanide is insoluble in strong alcohol, both methyl and ethyl.

about five hours, with frequent stirring, as the potassium cyanide and chloride settle to the bottom. The dark yellow mass, when cold, was extracted with chloroform, ether added to the filtered solution, and the precipitated mixture of chlorocaffeine and cyanocaffeine was purified by recrystallization from methyl alcohol. The product melted at 144°, and looked not unlike cyanocaffeine. But an estimation of chlorine and nitrogen showed that the mixture contained only about 30 per cent. of cyanocaffeine and 70 per cent. of chlorocaffeine. Here again all efforts to separate the two compounds completely, proved fruitless. In one instance, when the fusion was continued for fifty hours, the cyanocaffeine constituted about 60 per cent. of the mixture, but the product was very dark.

It would appear, from what has been said above, that the best method of preparing pure cyanocaffeine is by the dehydration of caffeinecarboxylamide by means of phosphorus pentoxide. Of the direct methods, the one of fusing chlorocaffeine with potassium cyanide, promises the best results; next to that, that of treating chlorocaffeine with potassium cyanide in methyl alcohol.

In concluding the description of the work upon cyanocaffeine, one more experiment, of an entirely different nature, may be mentioned: 2 grams of cyanocaffeine were dissolved in hot absolute amyl alcohol (B. P., 129°–131°) and to the boiling solution twice the calculated quantity of metallic sodium was added. The alcohol was removed by distilling, water added, the solution slightly acidulated with hydrochloric acid, and evaporated to dryness. The residue was exhausted with absolute ethyl alcohol. This, on concentrating, deposited a thick, brown, tarry mass, in which after two days standing, there appeared long, well-defined crystals imbedded in the dark mass. These crystals could not be freed entirely from the resinous material by water, alcohol, chloroform, or ether. It was shown to be a hydrochloride of an organic base. Unfortunately the substance could not be obtained of sufficient purity to allow a complete analysis.. But from its ready union with acids to form salts, its separation by alkalies, and its murexide-test, there is good reason to

think that the compound was most probably *caffeylmethylamine*, $C_8H_9N_4O_2(CH_3NH_2)$, formed by the reduction of the cyanide: $C_8H_9(CN)N_4O_2 + 4H = C_8H_9(CH_2NH_2)N_4O_2$.

SAPONIFICATION OF CAFFEINECARBOXYLAMIDE.

Hydroxycaffeine.—In preparing larger quantities of caffeinecarboxylamide by the method above described, the alcoholic filtrate from the insoluble acid-amide was in some instances concentrated, acidulated with hydrochloric acid, and evaporated to dryness. The residue was extracted with hot absolute alcohol. When cold, the alcohol gave a deposit of long white silky needles. These, when washed and dried, were found to be of a decidedly acid reaction, melting above 300°; insoluble in cold, but soluble in hot water. It was first taken for caffeinecarboxylic acid, $C_8H_9(COOH)N_4O_2$, but ultimate analysis showed that it was not that:

I. 0.0686 gram gave 0.1153 gram CO_2 + 0.0330 gram H_2O.
II. 0.2065 gram gave 50 cc. N at 22° and 746 mm.

	Calculated for $C_8H_9(OH)N_4O_2$.	Found. I.	Found. II.
C	45.71	45.83	....
H	4.76	5.33	....
N	26.66	....	26.65

Hydroxycaffeine was first obtained by E. Fischer[1] by heating bromocaffeine with alcoholic potash, and treating the resulting ethoxycaffeine with dilute hydrochloric acid.

$$C_8H_9(OC_2H_5)N_4O_2 + HCl = C_8H_9(OH)N_4O_2 + C_2H_5Cl.$$

The formation of hydroxycaffeine in connection with caffeinecarboxylamide can be accounted for in two ways: (1) potassium cyanide in itself may have induced the formation of ethoxycaffeine to some extent, and this, when treated with hydrochloric acid as above described, furnished hydroxycaffeine; (2) or, during concentration of the mother-liquor some of the potassium cyanide was changed into potassium carbonate; the latter acting upon the chlorocaffeine in solution, would tend to give ethoxycaffeine, which again would furnish hydroxycaffeine when evaporated with hydrochloric acid.

Decomposition by alkalies and acids.—Repeated trials with alcoholic potash or strong hydrochloric acid as saponifying

[1] *Loc. cit.*, **218**, 268.

agents, whether in open flasks or in sealed tubes at 100°–130°, have given only negative results. When potash was employed the compound often suffered complete decomposition into methylamine, ammonia, etc. The action of hydrochloric acid was variable, depending upon the temperature. On prolonged boiling in an open flask, or more rapidly at 120° in sealed tubes, the acid-amide was converted into caffeine with simultaneous formation of carbon dioxide.

$$C_6H_9(CONH_2)N_4O_2 + H_2O = C_8H_{10}N_4O_2 + CO_2 + NH_3.$$

At 160°–170° the caffeine in its turn suffered complete decomposition.[1] When the acid-amide was suspended in boiling absolute alcohol, and through the solution a stream of dry hydrochloric acid passed for many hours, there was no change whatever.

Estimation of the carbon dioxide liberated.—The acid-amide dissolves readily in concentrated sulphuric acid, also in dilute acid (1:1). On addition of water to the acid solution, the acid-amide separates out as a white amorphous powder, unchanged in composition; this is the best method for purifying caffeinecarboxylamide. But when the solution of the acid-amide in sulphuric acid (1:1) is heated on the the water-bath for about one-half hour, the whole of the caffeinecarboxylamide is converted into caffeine and carbon dioxide, according to the equation given above. Quantitative estimations of the amount of carbon dioxide thus set free were made, and the results fully confirmed the view expressed in the equation. The liberation of the gas begins at a little below 100°, but in order to gain time the temperature was raised to 130°.

I. 1.2810 grams gave 0.2411 gram CO_2.

II. 1.3065 grams gave 0.2372 gram CO_2.

	Calculated.	Found. I.	II.
CO_2	18.57	18.82	18.16

Caffeinecarboxylic Acid, $C_6H_9(COOH)N_4O_2$.—A solution of the acid-amide in sulphuric acid (1:1) was gently warmed at 75°–80° for a short time, and then water rapidly added to the acid; there soon came down a precipitate which consisted, as was found afterwards, of amorphous, unchanged acid-amide—with crystalline caffeinecarboxylic acid—and of caffeine. The

[1] E. Schmidt: Ann. Chem. (Liebig), **217**, 278.

precipitate, freed from sulphuric acid by filtration and washing, was treated with cold dilute alkali, which dissolved the caffeinecarboxylic acid and any remaining caffeine, leaving behind the caffeinecarboxylamide. On adding hydrochloric acid to the alkaline solution, there came down a copious precipitate of needle-like crystals. These were filtered off, washed with cold water and alcohol, and dried. They were analyzed with the following results:

I. 0.2794 gram gave 0.4667 gram CO_2 + 0.1094 gram H_2O.
II. 0.2612 gram gave 0.4390 gram CO_2 + 0.1035 gram H_2O.
III. 0.2531 gram gave 52.7 cc. N at 18° and 739 mm.
IV. 0.1530 gram gave 33 cc. N at 21° and 734 mm.
V. 0.1089 gram gave 22.8 cc. N at 18° and 740 mm.

	Calculated for $C_8H_9N_4O_2COOH$.	Found. I.	II.	III.	IV.	V.
C	45.38	45.56	45.88	....	....	....
H	4.20	4.35	4.40	....	....	....
N	23.53	....	....	23.88	24.22	24.05

Caffeinecarboxylic acid, when pure, has the following properties: White, silky, acicular crystals of sour taste, with a bitter aftertaste; melts at 225°–226°, with decomposition into caffeine and carbon dioxide; is of decidedly acid reaction, neutralizing alkalies and decomposing carbonates. It is insoluble in cold water and alcohol; soluble in these solvents when hot, with partial decomposition; insoluble in chloroform (unlike most caffeine compounds), carbon disulphide, and benzene; soluble in cold concentrated mineral acids without decomposition. It is an unstable acid, splitting off carbon dioxide with great facility when boiled with water or with dilute acids, or when heated by itself.

1.0234 grams of the acid, heated with dilute sulphuric acid, gave 0.1832 gram CO_2 = 17.90 per cent. 0.5198 gram, heated by itself to 150°, gave 0.0874 gram CO_2 = 16.83 per cent.,—the theoretical quantity being 18.57 per cent.

Methods of preparation.—The preparation of caffeinecarboxylic acid by the use of sulphuric acid is rather unsatisfactory, because of the small yield. In order to saponify all the acid-amide, the digestion has to be continued for some time, and the longer the digestion the more of the acid is likely to be

decomposed. Of the many methods tried, only a few need to be mentioned:

Nitric acid acts too violently, decomposing a considerable quantity of the carboxylic acid.

When the acid-amide is suspended in water, the calculated quantities of sulphuric acid and potassium nitrite added, and the flask set aside for days, there is no action whatever.

When the acid-amide is dissolved in sulphuric acid (50 per cent.) and to the cooled solution silver nitrate gradually added, there separates, on addition of water, a mixture of caffeinecarboxylic acid and a variable proportion of its silver salt. It is difficult to separate the free acid from the silver salt without considerable loss of the former.

When the acid-amide is dissolved in strong hydrochloric acid, in sulphuric acid of 50 per cent., or in sulphuric acid of 90 per cent., and set aside for two months, there is very little saponification. At the end of six months all the acid-amide was found to have disappeared and a fair yield of caffeinecarboxylic acid was obtained.

The method that proved most serviceable, however, was that based upon the use of nitrogen trioxide: The acid-amide is dissolved in sulphuric acid (1 : 1) and a stream of nitrogen trioxide is passed into the solution, till a few drops of the latter removed to a test-tube do not give any *amorphous precipitate* immediately on the addition of a little water, but a perfectly *crystalline* precipitate after a minute or two. When this stage has been reached, saponification is complete;

$$C_5H_3N_4O_2.CONH_2 + HNO_2 = C_5H_3N_4O_2CO_2H + H_2O + 2N.$$

The sulphuric acid is now largely diluted with water and set aside for complete precipitation. Caffeinecarboxylic acid, thus obtained, is white and pure, the yield being usually 85–90 per cent. of the theoretical quantity.

SALTS OF CAFFEINECARBOXYLIC ACID.

Caffeinecarboxylic acid, unstable in itself, readily forms salts of considerable stability. These salts are characterized by definite crystalline structure, and are obtained in the pure state without difficulty.

Sodium caffeinecarboxylate, $C_5H_3N_4O_2.CO_2Na.2H_2O$.—This

salt is prepared by adding sodium carbonate to a warm solution of the acid in water, evaporating to dryness, and extracting the residue with hot alcohol. On cooling, the salt separates out in fine white acicular crystals. It can also be prepared by neutralizing a solution of the acid with sodium hydrate (freshly prepared from the metal) and precipitating the salt with alcohol. The composition of the salt seems to be the same in both cases. It was dried between drying papers and analyzed with the following results:

I. 0.3487 gram gave on evaporation and ignition with sulphuric acid, 0.0826 gram Na_2SO_4.

II. 0.4128 gram gave 0.0965 gram Na_2SO_4.

	Calculated for $C_8H_9N_3O_3.CO_3Na.2H_2O$.	Found. I.	Found. II.
Na	7.77	7.68	7.58

The salt does not easily lose its water of crystallization; 0.5935 gram having lost only 0.0015 gram when heated in a water-bath for 2 hours. At 130° the loss is quite appreciable, and the water is completely driven off at 165°.

0.5933 gram salt lost at 165° 0.0769 gram water, and gave 0.1368 gram Na_2SO_4.

	Calculated.	Found.
H_2O	12.16	12.96
Na	7.77	7.47

The salt is very easily soluble in water and is soluble in hot alcohol. It is transposed by all mineral acids and also by acetic acid. On the addition of silver nitrate it gives a white gelatinous precipitate; when copper sulphate is added it gives a beautiful pale-green crystalline precipitate of copper caffeinecarboxylate; with ferric chloride it gives a dark red precipitate of a basic ferric salt.

Potassium salt, $C_8H_9N_4O_3.CO_2K.2H_2O$.—This salt is prepared in a manner similar to that of the sodium salt, which it resembles in appearance and behavior. It however loses its water of crystallization more readily than the sodium salt. The loss is appreciable when the substance is dried over sulphuric acid, and the salt thus becomes anhydrous in about two weeks. Most of the water is driven off at 100°, and all of it quite readily at 130°.

An air-dried sample was analyzed and furnished the following figures:

I. 0.4352 gram salt lost at 140° 0.0552 gram H_2O and gave 0.1187 K_2SO_4.

II. 0.6918 gram salt lost at 170° 0.0875 gram H_2O and gave 0.1897 gram K_2SO_4.

	Calculated for $C_8H_9N_4O_2.CO_2K.2H_2O$.	Found. I.	II.
H_2O	11.54	12.69	12.65
K	12.50	12.25	12.31

Calcium salt, $(C_8H_9N_4O_2.CO_2)_2Ca.5H_2O$.—The calcium salt was prepared by adding calcium carbonate to a warm solution of the acid, digesting on the water-bath and filtering off the excess of calcium carbonate while hot. On cooling, the calcium salt separates in long fine hair-like crystals, which grow rapidly and soon fill the beaker with a thick jelly-like mass. This was filtered and dried at a gentle heat to a constant weight. The salt does not lose in weight when heated for two hours in a steam-oven; the water of crystallization is driven off rapidly at 160° and completely at 170°. When subjected to analysis it yielded the following results:

I. 0.1719 gram salt dried over sulphuric acid to constant weight gave 0.0380 gram $CaSO_4$.

II. 0.4995 gram salt lost at 180° 0.0775 gram H_2O, and gave 0.1080 gram $CaSO_4$.

	Calculated for $(C_8H_9N_4O_2.CO_2)_2Ca.5H_2O$.	Found. I.	II.
H_2O	14.90	....	15.52
Ca	6.62	6.50	6.35

The salt is stable; does not break down at 200°. It is soluble in hot water, somewhat soluble in hot alcohol. It is decomposed by mineral acids.

Barium salt, $(C_8H_9N_4O_2.CO_2)_2Ba.5H_2O$.—The barium salt is prepared in a manner analogous to that of the calcium salt, or, by dissolving the acid in a warm solution of barium hydroxide, removing the excess of the latter with carbon dioxide, and concentrating the filtrate to crystallization. The salt separates readily in clusters of thick short acicular crystals, having the composition indicated above. The salt was analyzed with the following results:

I. 0.2535 gram salt dried over sulphuric acid to a constant weight, gave 0.0858 gram $BaSO_4$.

II. 0.4820 gram salt lost at 150° 0.0615 gram H_2O, and gave 0.1620 gram $BaSo_4$.

	Calculated for $(C_8H_9N_4O_2.CO_2)_2Ba.4H_2O$	Found. I.	II.
H_2O	12.84	....	12.74
Ba	19.52	19.90	19.75

Barium caffeinecarboxylate resembles the calcium salt very much, but it is less soluble in water, and still less in alcohol. It loses about 30 per cent. of its water of crystallization when heated in a steam-oven for several hours, and the remaining water is easily driven off at 150°.

Copper salt, $(C_8H_9N_4O_2.CO_2)_2Cu.4H_2O$.—When a solution of either potassium or sodium caffeinecarboxylate is added to a solution of copper sulphate, there comes down in a minute or two a precipitate of small, beautiful, glistening crystals. The salt was washed with water, alcohol, and ether, and dried at a gentle heat to a constant weight. The analysis of this salt gave these results:

I. 0.2992 gram salt gave 0.0381 CuO.

II. 0.5230 gram salt lost at 150° 0.0627 gram H_2O, and gave 0.0655 gram CuO.

	Calculated for $(C_8H_9N_4O_2.CO_2)_2Cu.4H_2O$.	Found. I.	II.
H_2O	11.82	....	11.99
Cu	10.39	10.19	10.02

The copper salt is of a pale green color, becoming emerald-green with loss of water. It is insoluble in either hot or cold water, or alcohol. It is soluble in dilute mineral acids and in acetic acid with decomposition.

Silver salt, $C_8H_9N_4O_2.CO_2Ag$.—When a solution of silver nitrate is added to a solution of caffeinecarboxylic acid, or to any of its soluble salts, a heavy gelatinous precipitate is at once thrown down, with almost quantitative precipitation of the silver. This precipitate, after careful washing and drying, was analyzed with the following results:

0.3258 gram gave 0.1052 gram Ag.

	Calculated for $C_8H_9N_4O_2.CO_2Ag$.	Found.
Ag	31.24	32.02

A much better method of preparing this salt is to add an ammoniacal solution of silver nitrate to a solution of caffeinecarboxylic acid in ammonia. On driving off the excess of ammonia, the silver salt comes down in a very pure crystalline form, easily washed and dried. When analyzed it furnished the following figures:

I. 0.2442 gram gave 0.2750 gram CO_2 + 0.0751 gram H_2O.

II. 0.1882 gram gave 28 cc. N at 24° and 741 mm.

III. 0.2943 gram gave 0.0923 gram Ag.

	Calculated for $C_8H_9N_4O_2.CO_2Ag$.	Found. I.	II.	III.
C	31.33	30.71	....	....
H	2.61	3.07	....	....
N	16.25	....	16.75	....
Ag	31.24	....	....	31.35

The silver salt is quite stable, is not transposed by comparatively strong nitric or sulphuric acid. When dry, it does not darken on exposure to sunlight for months. It is insoluble in either hot or cold water. Heated to 180°–200° it begins to sublime slowly, and at 270°, quite rapidly. The sublimate, however, contains no silver.[1]

Esters of Caffeinecarboxylic Acid.

Methyl Ester, $C_8H_9N_4O_2.CO_2CH_3$.—When silver caffeinecarboxylate is heated with the calculated quantity of methyl iodide in alcohol, at 100° or even on the water-bath with an inverted condenser, there soon separates the heavy silver iodide. The alcohol, filtered from the insoluble iodide, gives on cooling, a copious crystalline deposit of the methyl ester. This was purified by recrystallization from hot alcohol, dried to a constant weight, and analyzed with the following results:

I. 0.2014 gram gave 0.3555 gram CO_2 + 0.0965 gram H_2O.

II. 0.2577 gram gave 52.6 cc. N at 23° and 735 mm.

	Calculated for $C_8H_9N_4O_2.CO_2CH_3$.	Found. I.	II.
C	47.62	48.14	....
H	4.76	5.32	....
N	22.22	....	22.88

[1] A pure sample of the silver salt was washed with hot water to remove any remaining caffeinecarboxylic acid. It was then dried and washed with chloroform to free it entirely from caffeine. When carefully heated to 180°–200° it gave a sublimate of beautiful white, silky crystals, melting at 227° (M. P. of caffeine = 230°), and neutral in reaction. It is difficult to conceive how caffeine could be formed by the treatment above described. The compound which sublimed is not unlikely *dicaffeylketone*, $C_8H_9N_4O_2.CO.C_8H_9N_4O_2$.

The methyl ester is soluble in hot water with partial decomposition; is slightly soluble in cold alcohol, more readily in hot alcohol; easily soluble in chloroform; soluble in benzene; almost insoluble in ether. It begins to sublime undecomposed, without previously melting, at about 160°; melts sharp at 201.5° (uncorr). It does not break down when heated to above 200°, but is readily decomposed on boiling with dilute sulphuric acid:

$$C_7H_9N_4O_2.CO_2CH_3 + H_2O = C_7H_{10}N_4O_2 + CO_2 + CH_3OH.$$

Ethyl Ester, $C_7H_9N_4O_2.CO_2C_2H_5$.—This ester is prepared in exactly the same way as the corresponding methyl salt, which it closely resembles in appearance. Prepared and purified as described under methyl ester, it gave, on analysis, the following figures:

0.1768 gram gave 0.3272 gram CO_2 + 0.0854 gram H_2O.

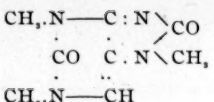
	Calculated for $C_7H_9N_4O_2.CO_2C_2H_5$.	Found.
C	49.62	50.46
H	5.26	5.36

The ethyl ester is soluble in the different solvents to about the same extent as the methyl salt. It sublimes undecomposed at about 160° and melts at 207°–208°. Like the methyl ester it is not decomposed when heated to a temperature above 200°, but is readily decomposed when heated with dilute acids.

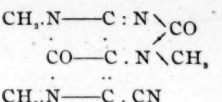
Attempts to prepare the corresponding *phenyl* ester proved unsuccessful. The silver salt was heated with brombenzene dissolved in benzene at 170° for several hours, but showed no change. Samples were then heated with iodobenzene at 200° for about fifteen hours. The contents of the tube were found to contain a great deal of unchanged silver caffeinecarboxylate and some silver oxide. There was also separated a small crop of crystals containing no silver. An estimation of nitrogen showed that it was not the phenyl ester. This body resembled very much the crystals obtained by the sublimation of the silver salt (p. 418).

Summary.

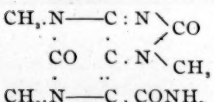
All the new compounds described in this paper present the interesting feature, that they are the first compounds of caffeine in which the carbon of the CH group has been linked directly to a new carbon atom.



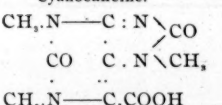
Caffeine.



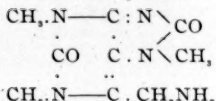
Cyanocaffeine.



Caffeinecarboxylamide.



Caffeinecarboxylic acid.



Caffeylmethylamine (?).

The preparation of these compounds was not undertaken with any view to either confirm or disprove the accepted structural formula of caffeine. But, as far as they go, the properties of these compounds are explained by E. Fischer's formula of caffeine quite satisfactorily.

In a previous paper[1] attention was called to the difficulty of converting bromocaffeine and chlorocaffeine into the corresponding iodo-compound by the usual treatment with the iodides of potassium, sodium, and calcium. This pointed to the tertiary nature of the CH group. The experience with mercuric cyanide and the double cyanide of mercury and potassium suggests the same view.

The instability of the carboxylic acid, and the comparative stability of its esters, is an interesting feature of this compound. This fact is in accord with the general nature of many acids in which the carboxyl is linked to an unsaturated carbon atom $\left(\diagup\!\!\diagdown C.CO_2H\right)$. A large number of such acids split off carbon dioxide more or less readily on heating. The close proximity of the nitrogen atom will also tend to make this an unstable acid $\left(N.\overset{\|}{C}.CO_2H\right)$, as is the case with some amido-acids.

CHEMICAL LABORATORY,
UNIVERSITY OF MICHIGAN.

[1] This Journal, 14, 614.

Contributions from the Chemical Laboratory of the Rose Polytechnic Institute.

XII.—CAMPHORIC ACID.

THIRD PAPER.

By W. A. Noyes.

In my last paper[1] it was shown that di-hydroamino-campholytic acid yields campholytic acid when treated with nitrous acid. A further study of the reaction has shown that there is also formed, at the same time, a hydroxy acid which evidently contains the hydroxyl group in the same position as the amino group of the acid from which it is derived. This acid possesses quite unusual interest, since, in conjunction with other compounds and relations which will be discussed in this paper, it furnishes quite conclusive proof that the carboxyl groups of camphoric acid are combined with adjacent carbon atoms. Two distinct lines of proof lead to this conclusion. One was first pointed out by Walker[2] and depends on the conduct of the di-bromide of campholytic acid, which indicates that the double union in that acid is in the $\alpha\,\beta$ position. This conclusion has received a further confirmation by a study of the conduct of campholytic acid toward dilute sulphuric acid. Fittig has shown[3] that dilute sulphuric acid converts $\beta\,\gamma$ acids into the corresponding lactones while $\alpha\,\beta$ acids are not affected. Dilute sulphuric acid changes campholytic acid, it is true, *but does not convert it into a lactone.* It may be objected that the reactions which Fittig has established for unsaturated acids with an open chain do not necessarily hold good for cyclic compounds, but it will be shown in this paper that the reaction in question does convert an isomeric acid into a lactone.

The second proof that camphoric acid contains the two carboxyls combined with adjacent carbon atoms consists in the fact that the hydroxy acid which has been referred to cannot be converted into a lactone by the action of dilute acids. At least four lactones derived from camphoric acid are known; the campholactone of Fittig and Woringer[4], an isomeric lac-

[1] This Journal, **16**, 505.
[2] J. Chem. Soc., **63**, 510 (1893).
[3] Ber. d. chem. Ges., **27**, 2667.
[4] Ann. Chem. (Liebig), **227**, 10.

tone to be described in this paper, camphanic acid[1], and a brom-lactone mentioned by Aschan[2]. This shows that the presence of the ring does not interfere with the formation of lactones and furnishes almost positive proof that the hydroxyl of the hydroxy acid which I have obtained is not in the γ position with regard to the carboxyl. The only other relations possible in a pentamethylene or hexamethylene ring are the α, β, and δ positions for the hydroxyl. The δ position is inconsistent with the formation of camphoric anhydride and the α position does not agree with the differences observed in the decompositions of the two amino acids, to mention only one of many facts which could be brought forward against it. The main argument in favor of the γ position rests on the formation of camphanic acid and campholactone from brom-camphoric anhydride. But this compound loses hydrobromic acid readily,[3] giving an unsaturated acid which must have the double union in the β γ position, if the reasoning given above is correct, and such an acid would then give, by rearrangement, a lactone in accordance with the reaction so often observed by Fittig and his co-workers.

If the conclusion which I have reached is accepted, the formula proposed by Bredt[4] for camphoric acid must be considered as definitely disproved. That the conduct of campholytic acid is not consistent with the tetramethylene formula of Ballo[5] was pointed out by Walker.[6]

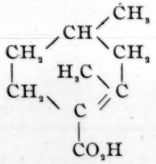
When campholytic acid is allowed to stand with dilute sulphuric acid for some time it is converted quantitatively into an isomeric, solid acid. Di-hydro-hydroxy-campholytic acid is converted, even more easily, into the same acid by the action of dilute sulphuric acid, but it may be converted, in part, at least, into the first campholytic by conversion into a hydrobromide and by treating the latter with caustic soda. The transformation of the campholytic acid may also be effected by means of hydrobromic acid, but less readily. The new acid has been already described by Walker[7] under the name of camphothetic acid and was considered by him as having the composition

[1] *Ibid*, **172**, 151.
[2] Ber. d. chem. Ges., **27**, 3505.
[3] Aschan: Ber. d. chem. Ges., **27**, 3506.
[4] Ber. d. chem. Ges., **26**, 3049.
[5] *Ibid*, **14**, 337.
[6] *Loc. cit.*
[7] J. Chem. Soc., **63**, 504 (1893).

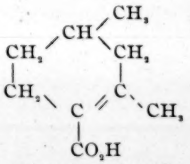
$C_8H_{14}CO_2H$
|
$C_8H_{14}CO_2H$. Dr. Walker has very kindly sent me a small specimen of his acid, and its conduct toward permanganate, crystalline form, and melting-point, leave no doubt that the acids are identical. The proofs for the formula $C_8H_{13}CO_2H$ will be given below.

The facts that the new acid is formed directly from dihydro-hydroxy-campholytic acid and that it is not converted into a lactone by dilute sulphuric acid compel us to the conclusion that the double union in the acid is in the $\alpha\beta$, or Δ^1 position. But the double union in the first campholytic acid is also in the Δ^1 position.

These relations can, I think, be satisfactorily explained by the following formulæ.



Cis-trans-campholytic acid.



Cis-campholytic acid.

The configuration represented by the second formula would undoubtedly be the more stable and this is assigned to the new acid. The cis-trans formula here given has been discussed for a similar case by Baeyer[1] and has been dismissed as improbable because of the tension within the molecule to which it would give rise. If the formula is followed by means of models, however, it will be seen that there is a position in which the carboxyl and methyl groups are outside of the plane of the ring which gives rise to less tension than is found in a tetramethylene ring.

It may be objected to the formulæ given that the double union in the two acids might be in the Δ^1 and Δ^6 positions respectively. But this would be inconsistent with the fact that in the addition of hydrobromic acid the bromine appears

[1] Ann. d. Chem. (Liebig), **258**, 156.

always to take the β position.[1] Since the Δ^6 compound could only be formed from a bromine derivative having the bromine in the α position.

It has been assumed in several recent discussions of unsaturated cyclic compounds that stereoisomerism is impossible for the Δ^1 position. I believe, however, that there is already one case on record where there is an indication of such isomerism. In the study of Δ^1 tetrahydro-benzoic acid Aschan[2] observed a solid and a liquid acid which apparently bore to each other a relation very similar to that observed in the case of the campholytic acids. On account of the importance of the question, it is intended to examine the case more fully and it is hoped that further proof in support of these formulæ may be obtained. Meanwhile I believe that the dogma with regard to the sterioisomerism of Δ^1 compounds should be used with some caution.

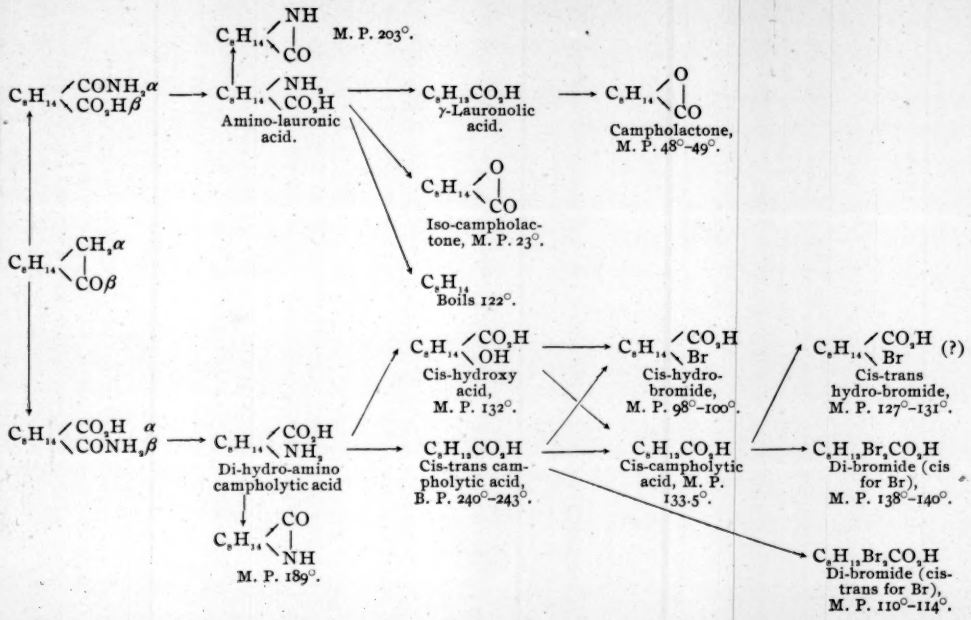
By the use of models it becomes evident at once that the cis-trans-campholytic acid would give a hydrobromide in which the bromine and carboxyl are in the "cis" position. Since, as will be shown, the di-hydro-hydroxycampholytic acid gives the same hydrobromide, it follows that this is a "cis" compound and further that ordinary camphoric acid itself is a "cis" compound. This conclusion was reached some time ago by Aschan.[3]

In this discussion it is not intended to imply that the presence of a hexamethylene ring in camphoric acid is considered as definitely proved. The reasoning given will apply also to a pentamethylene ring, though it must be admitted that a cis-trans, Δ^1 compound in a pentamethylene ring is not as probable as in a hexamethylene compound. The relationships which have been established thus far in my work will be clear from the accompanying table.

Di-hydro-hydroxycampholytic Acid.

The decomposition of di-hydro-amino-campholytic acid with nitrous acid is best effected as follows. 20 grams of the acid are dissolved in 19 cc. of dilute sulphuric acid (1:5) and 60 cc. of water, the solution is cooled and the calculated amount

[1] See Baeyer: Ann. Chem. (Liebig), **269**, 156. [2] *Ibid.* **271**, 270.
[3] Ber. d. chem. Ges., **27**, 2002.


M. P. 203°.
Amino-lauronic acid.
γ-Lauronolic acid.
Campholactone, M. P. 48°–49°.
Iso-campholactone, M. P. 23°.
Boils 122°.
Cis-hydroxy acid, M. P. 132°.
Cis-hydro-bromide, M. P. 98°–100°.
Cis-trans hydro-bromide, M. P. 127°–131°.
Di-hydro-amino campholytic acid
Cis-trans campholytic acid, B. P. 240°–243°.
Cis-campholytic acid, M. P. 133·5°.
Di-bromide (cis for Br), M. P. 138°–140°.
M. P. 189°.
Di-bromide (cis-trans for Br), M. P. 110°–114°.

of a 20-per cent. solution of sodium nitrite is introduced carefully at the bottom of the flask by means of a pipette. If the sodium nitrite is added carelessly there is a considerable loss of oxides of nitrogen but, if the solution is added as stated, the reaction takes place slowly and with very little escape of nitrous fumes. When the reaction is nearly complete more sulphuric acid is added and the whole is allowed to stand as long as the evolution of nitrogen continues. The campholytic acid and part of the hydroxy acid separate as an oil. The whole is extracted two or three times with small quantities of ligroin, which dissolves the campholytic acid easily but leaves most of the hydroxy acid undissolved. The latter is then extracted from the solution with ether. The residue left on distilling the ether is recrystallized from water, or, better, from acetic ether.[1] The acid crystallizes in compact small crystals which melt at 132°. It is moderately soluble in water and ether, very difficultly soluble in ligroin, easily soluble in alcohol. The aqueous solution is stable toward potassium permanganate. Beckman's mixture[2] of sulphuric acid and potassium pyrochromate is without effect on the acid in the cold, and even on warming darkens but very slowly with it, indicating that the hydroxyl group is tertiary. This agrees with the interpretation which has been given of the decomposition of amino-lauroic acid,[3] which must have the carboxyl group in the same position as the hydroxyl group in this acid. The acid gives with fuming hydrobromic acid the same hydrobromide, melting at 98°–100°, which is obtained from the cis-trans-campholytic acid. This hydrobromide is believed to be a "cis" compound for reasons which have been given. When the hydroxy acid is warmed with dilute sulphuric acid (1 : 1), or more slowly on simply standing with it in the cold, it is converted quantitatively into cis-campholytic acid. In spite of the ease with which this change takes place the free hydroxy acid may be distilled in a small tube with only a very trifling decomposition, the distilled acid being insoluble in ligroin and almost perfectly stable toward permanganate. The analyses of the acid were as follows:

[1] See Einhorn and Meyenberg: Ber. d. chem. Ges., **27**, 2472.
[2] Ann. Chem. (Liebig), **250**, 325. [3] This Journal, **16**, 509.

0.1458 gram of the acid gave 0.1224 gram H_2O and 0.3329 gram CO_2.

0.1450 gram of the acid gave 0.1212 gram H_2O and 0.3344 gram CO_2.

	Calculated for $C_8H_{14}\langle^{CO_2H}_{OH}$	Found. I.	II.
C	62.79	62.27	62.90
H	9.30	9.33	9.29

Cis-trans-Campholytic Acid.

This acid was first prepared by Walker,[1] and was referred to in my last paper. The acid has now been further characterized by the preparation of the hydrobromide and by its conversion into cis-campholytic acid.

Hydrobromide of Cis-trans-campholytic Acid.
(Cis-β-brom-di-hydrocampholytic Acid.)

This acid is formed from either di-hydro-hydroxy-campholytic acid or cis-trans-campholytic acid by treatment with fuming hydrobromic acid and a little ligroin. The acid separates very soon in crystalline form and may be filtered on asbestos and washed with *cold* water. It must be dried at once *in vacuo* to prevent decomposition. It is stable in dry air, but decomposes slowly in moist air. It may be dissolved in cold ligroin and crystallized by evaporation under diminished pressure. It then separates in small aggregates of rectangular plates. The acid is decomposed at once by alkalies, chiefly with the formation of cis-trans-campholytic acid. There is formed, at the same time, a small amount of an indifferent body, probably a hydrocarbon. Fittig[2] has shown that this decomposition is characteristic of acids having bromine in the β-position. The acid melts, with decomposition, at 98°–100°. The cis position for bromine and carboxyl follows from the relation of the acid to cis-trans-campholytic acid.

0.1141 gram of the acid prepared from cis-trans-campholytic acid gave 0.0912 gram AgBr.

0.0176 gram of the acid prepared from the hydroxy acid gave 0.0141 gram Ag Br.

	Calculated for $C_8H_{14}\langle^{CO_2H}_{Br}$	Found. I.	II.
Br	34.04	34.01	34.09

[1] J. Chem. Soc., **63**, 488, (1893). [2] Ber. d. chem. Ges., **27**, 2662.

Cis-Campholytic Acid.
(*Walker's Camphothetic Acid.*)

The formation of this acid was first observed when campholytic acid had been left for some time in contact with hydrobromic acid, and an attempt was made to crystallize the product obtained from warm ligroin. Soon afterwards, on boiling cis-trans-campholytic acid with dilute sulphuric acid, as Fittig[1] directs for $\beta\gamma$ unsaturated acids, it was found that the same product is formed. At a high temperature the transformation is accompanied by a considerable amount of decomposition. The transformation may be made almost quantitative by leaving cis-trans-campholytic acid in contact with dilute sulphuric acid (1 : 1) at ordinary temperatures for some days. The acid is best crystallized from alcohol, in which it is quite easily soluble. It separates from that solvent in long thick needles. From ligroin it crystallizes in rectangular plates, as was observed by Walker.[2] The acid is very difficultly soluble in water, one part of the acid requiring 5880 parts of water for its solution at 20°. It is easily soluble in ether. The molecular weight was determined by the depression of the freezing point of acetic acid.[3]

0.2584 gram of the acid dissolved in 9.247 grams acetic acid caused a depression of 0.70°.

0.4446 gram of the acid caused a depression of 1.17°.

	Calculated.	Found. I.	Found. II.
Mol. W.	154	155.6	160.2

That the acid is a true unsaturated acid and not the isomeric lactone is proved by the fact that it dissolves readily and completely in a cold solution of sodium carbonate and the solution decolorizes potassium permanganate instantly, while the lactones of this series are stable towards that reagent. The acid melts at 133.5°. The first analyses were with an acid crystallized from dilute alcohol and were not satisfactory. The last three were with an acid crystallized from ligroin.

[1] Ber. d. chem. Ges., **27**, 2667.

[2] J. Chem. Soc., **63**, 504.

[3] In a private communication Dr. Walker states that he has obtained with benzene the values 182 and 190 (theory 182) for the molecular weight of the ethyl ester. The values in his paper were obtained by a student, and are evidently erroneous.

0.1768 gram gave 0.1475 gram H_2O and 0.4498 gram CO^2.
0.1580 " " 0.1306 " " " 0.4012 " "
0.1780 " " 0.1455 " " " 0.4526 " "
0.1641 " " 0.1345 " " " 0.4201 " "
0.0869 " " 0.0726 " " " 0.2223 " "

	Calculated for $C_8H_{13}CO_2H$	Found. I.	II.	III.	IV.	V.
C	70.13	69.38	69.25	69.44	69.82	69.77
H	9.09	9.27	9.18	9.08	9.10	9.28

The last analysis was made with an acid obtained by the action of hydrobromic acid on the cis-trans-campholytic acid.

The *barium* salt of the acid is described by Walker[1] as containing five molecules of water. I have not been able to obtain a salt of that composition. The salt deposited from the hot solution during evaporation on the water-bath contains very little water, one and one-half per cent. being found. The salt deposited on cooling the hot solution contains water of crystallization but loses it so readily in a warm room that the number of molecules present could not be satifactorily determined. In two cases the salt pressed between filter-paper lost 27.37 per cent. and 20.76 per cent. at 135°. Nine molecules of water would correspond to 26.78 per cent.

0.0780 gram of the salt dried at 135° gave 0.0405 gram $BaSO_4$.

	Calculated for $(C_8H_{13}CO_2)_2Ba$.	Found.
Ba	30.92	30.94

After the work described in this paper had been completed, the possibility suggested itself that the cis-campholytic acid here described might be identical with the iso-lauronolic acid of Koenigs and Hoerlin.[2] The oxidation of the acid with potassium permanganate gave isolauronic acid,[3] melting at 134° (Koenigs and Meyer gives 132°) and the latter gave the yellow phenylhydrazide, melting at 199°, thus establishing the identity of the two acids beyond question, though some of the statements of Koenigs and Hoerlin do not agree very well with my observations. The iso-lauronic acid obtained was analyzed.

[1] *Loc. cit.* [2] Ber. d. chem. Ges., **26**, 814. [3] *Ibid*, **27**, 3467.

0.1672 gram gave 0.1093 gram H_2O and 0.3918 gram CO_2.

	Calculated for $C_8H_{12}O_3$.	Found.
C	64.28	63.91
H	7.14	7.26

As Koenigs and Hoerlin seem to be in doubt whether their acid may not be a lactone, and did not obtain correct values for an unsaturated acid in their analyses of salts, the calcium salt has been prepared and analyzed. The salt is decomposed by carbon dioxide, as stated in their paper, and in preparing it care is required to prevent its contamination with the free acid. The salt is deposited, on evaporating its solution in vacuo, in fine needles which lose their water easily over sulphuric acid. The salt, air-dried for a very short time, gave the following results:

0.0377 gram lost 0.0059 gram H_2O at 135° and gave 0.0121 gram $CaSO_4$.

0.0832 gram lost 0.0131 gram H_2O at 135° and gave 0.0273 $CaSO_4$.

	Calculated for $(C_8H_{13}CO_3)_2Ca+3\frac{1}{2}H_2O$.	Found. I.	Found. II.
$3\frac{1}{2}H_2O$	15.40	15.65	15.74
Ca	9.78	9.44	9.64

As I have shown the close relation which exists between campholytic acid and this acid, and as I have discovered another acid which bears a similar close relation to lauronolic acid, it seems desirable to name this acid iso-campholytic acid or cis-campholytic acid, and to give the name iso-lauronolic acid to the acid described in the latter part of this paper.

Di-bromide of Cis-campholytic Acid.

Two grams of the cis-campholytic acid were dissolved in a small amount of chloroform and the solution was cooled with a freezing mixture. A little more than the theoretical amount of bromine, dissolved in a little chloroform, was added slowly and the whole allowed to stand for a short time. The chloroform was then evaporated under diminished pressure, a little ligroin added, and the evaporation repeated till the bromide separated in crystalline form. As thus prepared, the acid consists of microscopic white crystals, which are very difficultly soluble in ligroin. There is formed, also, a considerable

quantity of an oil which is easily soluble in ligroin. The acid melts with decomposition at 138°–140°. The dibromide is decomposed by a solution of sodium carbonate with the separation of an indifferent body which is insoluble in caustic soda. This decomposition is characteristic of $\alpha\beta$ dibrom acids.

0.1152 gram of the acid gave 0.1391 gram AgBr.

0.1022 gram of the acid gave 0.1224 gram AgBr.

	Calculated for $C_8H_{13}Br_2CO_2H$.	Found. I.	Found. II.
Br	50.95	51.38	50.97

Hydrobromide of Cis-campholytic Acid.
(*Cis-trans-β-brom-di-hydro-campholytic Acid.*)

In one instance there was obtained by the action of fuming hydrobromic acid on cis-campholytic acid a hydrobromide which melted at 127°–130° and which gave, on analysis, 34.85 per cent. of bromine. Repeated attempts to obtain the same acid a second time were unsuccessful, though the conditions were varied, and in one case glacial acetic acid saturated with hydrobromic acid was used. An acid melting at 110°–115° was obtained several times and in one case was analyzed, giving 32.89 per cent. of bromine. Theory requires 34.04 per cent. Recrystallization from ligroin did not change the melting of either specimen. Solution in warm glacial formic acid caused the specimen melting at 110°–115° to decompose. It is evident that the acid combines with hydrobromic acid with difficulty, but it is believed that the body melting at 127°–130° consisted chiefly of the true hydromide of the acid.

Many attempts have been made with each of the campholytic acids to obtain from them benzene derivatives by heating in sealed tubes with the calculated amouut of bromine in accordance with the method which has been used successfully by Einhorn and Willstätter.[1] Even at 100° the bromine is completely decolorized, but no simple reaction-product could be obtained. At temperatures approaching 200° there was a considerable amount of carbonization. I attach little weight to the negative result as bearing on the constitution of camphoric acid.

[1] Ann. Chem. (Liebig), **280**, 88.

Hydrocarbon C_8H_{14}.

In my last paper it was stated that the decomposition of amino-laronic acid with nitrous acid yields an unsaturated acid, a lactone, a hydrocarbon, and carbon dioxide. The products have now been more carefully studied. Approximately 10 per cent. of the amino acid is decomposed in such a manner as to yield the hydrocarbon. The body is a clear, colorless liquid with a turpentine-like odor. It boils at 122°. Its specific gravity is 0.8033 at 15° and 0.8004 at 20°, referred, in each case, to water at the same temperature. It is probably the same hydrocarbon as that recently observed by Aschan,[1] but different from that of Koenigs and Meyer.[2]

0.1016 gram gave 0.1169 gram H_2O and 0.3240 gram CO_2.

	Calculated for C_8H_{14}.	Found.
H	12.63	12.68
C	87.27	86.97

When 4 atoms of bromine are added carefully to the hydrocarbon and the mixture is heated to 200° in a sealed tube the whole is carbonized. This resembles the conduct of some pentamethylene derivatives as observed by Perkin,[3] but when we recall the conduct of turpentine toward bromine[4] the result cannot be considered as important.

Iso-campholactone.

This body has not been obtained in sufficient amount for a satisfactory analysis. It has, however, been thoroughly characterized as a lactone by its insolubility in sodium and potassium carbonates, by conversion into the barium salt of the corresponding hydroxy acid, and by regeneration on boiling the latter with dilute hydrochloric acid. The body may be crystallized, at a low temperature, from a very little ligroin. It melts at 23° and is, therefore, isomeric and not identical with the campholactone of Fittig and Woringer.[5] At it will be shown that γ-lauronolic acid can be converted into the latter lactone, the two lactones are probably stereoisomers. Both lactones are stable toward potassium permanganate.

[1] Ber. d. chem. Ges., **27**, 3507.
[2] *Ibid*, **27**, 3470.
[3] J. Chem. Soc., **51**, 247, and **65**, 979.
[4] See Kekule: Ber. d. chem. Ges., **6**, 438.
[5] Ann. Chem. (Liebig), **227**, 10.

γ-Lauronolic Acid.

This acid was described in my last paper and the analysis of its calcium salt was given. A name was not given to the acid as it then seemed possible that the acid was identical with the lauronolic acid of Woringer.[1] The latter acid has recently been prepared by Aschan[2] and the fact that its calcium salt contains 3 molecules of water has been confirmed, and the acid been further characterized by the preparation of its amide. As in both respects the acid differs from that which I have obtained, the two acids must be considered as isomeric. The new acid would naturally be named iso-lauronolic acid but, unfortunately, this name has already been given to another acid by Koenigs[3] and the name γ-lauronolic acid appears to be the best available, unless the name of Koenigs' acid is changed as suggested in this paper and as seems desirable.[4]

When the acid is warmed on the water-bath and shaken for a short time with dilute sulphuric acid, it is converted in part, into the campholactone of Woringer. This characterizes the acid as a β γ unsaturated acid.

The amide was prepared as follows: The dry acid, obtained from the crystallized calcium salt, was cooled with a freezing mixture, and a little more than the theoretical amount of phosphorus pentachloride was added. After the reaction was complete the products were poured carefully into cooled aqueous ammonia (0.90). The amide which separated would not solidify at —20° though it became very viscous. From the solution in water it separated, on spontaneous evaporation, in oily drops. It was shown by analysis that the amide had really been formed.

0.1016 gram of the amide gave 0.00897 gram N.

	Calculated for $C_8H_{13}CONH_2$.	Found.
N	9.15	8.83

1 *Ibid*, **227**, 6.

2 Ber. d. chem. Ges., **27**, 3504.

3 Ber. d. chem. Ges., **27**, 3346, and **26**, 814.

4 γ-Lauronolic acid has also been described and further characterized by Walker and Henderson under the name of allo-campholytic acid (J. Chem. Soc., *1895*, 341).

Campholactone.

This is formed when γ-lauronolic acid is warmed at 100° for a short time with dilute sulphuric acid. It was purified by shaking with a solution of potassium carbonate and conversion into the barium salt of the corresponding hydroxy acid. The latter was analyzed.

0.2209 gram of the salt dried at 105° gave 0.1056 gram $BaSO_4$.

	$\left(C_8H_{14}{<}^{OH}_{CO_2}\right)_2Ba$.	Found.
Ba	28.60	28.12

The lactone, regenerated from the salt, melted at 48°–49° and is undoubtedly identical with the campholactone of Woringer.[1] As he states that lauronolic acid is also formed when the lactone is regenerated from its salts the close connection between γ-lauronolic acid and lauronolic acid is established. The two acids are probably stereoisomers.

Several attempts have been made to secure the hydroxy acid corresponding to amino-lauronic acid but without success. Possibly, because its hydroxyl group would be that of a secondary alcohol, it is easily oxidized. In one case a small amount of an acid which melts at about 180° was obtained. A combustion made with a not very pure specimen of the acid gave 50.79 per cent. carbon and 6.88 per cent. hydrogen.

Possibly this is $CH_3-\underset{\displaystyle CO_2H}{\overset{\displaystyle CO_2H}{\underset{|}{\overset{|}{C}}}}-CH_2-\underset{|}{\overset{|}{CH}}-CH_2-CO_2H$, which would be formed by the oxidation of lauronolic acid if it has the formula which I have spoken of as probable. Such an acid would require 49.54 per cent. carbon and 6.42 per cent. of hydrogen. A study of the oxidation products of γ-lauronolic acid may throw further light on the matter.

TERRE HAUTE. February 26, 1895.

[1] *Loc. cit.*

Contribution from the Kent Chemical Laboratory of the University of Chicago.

ON SOME EXPERIMENTS WITH ACETYLACETONE AND ACETACETIC ETHER.

By Richard S. Curtiss.

Nef has shown[1] that when silver acetylacetone is treated with ethyl iodide, an oil is obtained which is a mixture of two products; the one is neutral, the other soluble in sodium hydroxide, and the boiling-point of each is 175°–180°. I have carried out the experiment with larger quantities, and analyzed both products thus obtained.

α-Acetyl-β-ethoxypropylene, $\begin{matrix} CH_3COC_2H_5 \\ \vdots \\ HCCOCH_3 \end{matrix}$.

The silver salt was prepared by adding concentrated aqueous argentic nitrate (one molecule) to an ice-cold aqueous solution of sodium acetylacetone (1:6). The silver salt has all the properties ascribed to it by Nef. 87 grams were obtained from 65 grams of sodium salt.

The silver salt (27.2 grams) was added to an excess of ethyl iodide (35 grams), care being taken to keep the temperature below 30°. After standing for 30–35 hours, the excess of ethyl iodide was distilled off, and the residue extracted with ether. The acid products of the reaction were extracted from the ethereal filtrate by means of dilute sodic hydrate (at 0°), and the alkaline solution, acidified and extracted with ether, gave 4 grams of an oil, which was found to be a mixture of acetylacetone and of α-ethylacetylacetone, (see below).

The ethereal solution, containing only the neutral products of the reaction, was found to contain an oil (4 grams), boiling between 68° and 70° at 15 mm. pressure. The oil thus obtained tenaciously holds small quantities of ethyl iodide, as shown by analysis, which can only be removed by repeated fractional distillation, or by digestion with a small amount of silver acetylacetone.

A product distilled twice and boiling at 71.5°–72° at 15 mm. pressure, gave the following results on analysis:

[1] Ann. Chem. (Liebig), **277**, 73.

0.2084 gram substance gave 0.4961 gram CO_2 and 0.1790 gram H_2O.

	Theory for $C_7H_{12}O_2$.	Found.
C	65.62	64.92
H	9.37	9.54

The substance obtained is thus a mono-ethylated acetylacetone. It is a neutral oil with fragrant odor, turning light green on standing. From its properties there can be no doubt that the substance is α-acetyl-β-ethoxypropylene, formed from silver acetylacetone by the direct replacement of the silver atom. The substance reacts with great violence with bromine in dilute chloroform solution and hydrobromic acid is evolved, but no study was made of the products formed.

The acid products (4 grams), formed by the action of ethyl iodide on silver acetylacetone, are acetylacetone and α-ethylacetylacetone. These can be separated by shaking in ether solution with aqueous sodium carbonate (at 0°), in which the former substance—a much stronger acid than the latter—dissolves. The acetylacetone obtained boiled at 140°–141° and was converted into the copper salt, (m. p. above 270°). The part insoluble in soda, after two distillations at reduced pressure, boiled at 64°–67° at 12–15 mm. pressure, and gave the following figures on analysis:

0.2548 gram substance gave 0.6109 gram CO_2 and 0.2212 gram H_2O.

	Theory for $C_7H_{12}O_2$.	Found.
C	65.62	65.39
H	9.37	9.64

This substance α-ethylacetylacetone has already been obtained by Combes[1] from sodium acetylacetone and ethyl iodide (by heating in a sealed tube to 140°). In addition to the properties mentioned by Combes, which were confirmed, it forms, on shaking with aqueous copper-acetate solution, a well-defined copper salt. The salt is insoluble in water; nearly so in ligroin; very slightly soluble in cold alcohol, ether, carbon bisulphide, and benzene, but much more readily soluble on

[1] Ann. chim. phy., [6] **12**, 247.

warming. It is easily soluble in cold chloroform. For the analysis it was crystallized from hot alcohol, from which it separates out, on cooling, in long silky greyish-green needles, or in hair-like threads. It melts at 210°–212° with previous browning at 205°.

Analysis: 0.3184 gram substance gave 0.0793 gram Cu_2S.

	Theory for $C_{14}H_{22}O_4Cu$.	Found.
Cu	19.92	19.89

The only logical and consistent explanation possible of the action of ethyl iodide on silver acetylacetone, $CH_3.COAg$ $HC.COCH_3$, is the following: The molecule has two points about equally susceptible of attack, namely, the silver atom, and the double bond between the two carbon atoms. In consequence thereof a direct replacement of the silver by ethyl takes place, as well as an addition of ethyl iodide to doubly bound carbon atoms,[1] resulting thus in the formation of α-acetyl-β-ethoxypropylene and α-ethylacetylacetone.

The Action of Hydrochloric Acid and Alcohol on Acetacetic Ether.

Notwithstanding the fact that Nef has clearly demonstrated the close analogy existing between the oxymethylene compounds and acetacetic ether in the free state, Claisen in a later paper[2] still maintains, without any apparent reason, his former position, that these compounds behave in a totally different manner. The points of difference brought forward by Claisen have been met *seriatim* and fully[3] by the experiments of Nef and Bernhard[4]—with one exception: Claisen states that his oxymethylene compounds, like the fatty acids, are converted by means of hydrochloric acid and alcohol into their esters. I have therefore undertaken, at the suggestion of Dr. Nef, to show that the same is true of acetacetic ether:

66 grams acetacetic ether (1 molecule) were dissolved in 12 molecules of absolute alcohol and a steady current of dry hydrochloric acid gas passed, for ten minutes, into the solu-

[1] Nef: Ann. Chem. (Liebig), **276**, 200; **277**, 59.
[2] Ann. Chem. (Liebig), **281**, 311.
[3] Ann. Chem. (Liebig), **276**, 238.
[4] Ann. Chem. (Liebig), **282**, 173, 177.

tion cooled to —10°. After standing for forty-eight hours at ordinary temperature, the mixture is poured into much cold water, extracted with ether, the ethereal solution well washed with ice-cold sodic hydrate, and then dried with fused potassium carbonate. After distilling off the ether a yellow, fragrant oil is left, which, on cooling, solidifies. Large colorless, tabular crystals were obtained, melting at 30°, identical in every respect with Friedrich's β-ethoxycrotonic ether.[1]

Analysis.—0.1843 gram substance gave 0.1479 gram H_2O, and 0.4097 gram CO_2.

	Theory for $C_8H_{14}O_3$.	Found.
C	60.76	60.63
H	8.86	8.91

The yield obtained in the above experiment was 15 per cent. of the acetacetic ether taken. In another experiment where 6 molecules of alcohol were used to one of acetacetic ether, and anhydrous copper sulphate was present as a dehydrating agent, the same yield was obtained.

Freer has shown[2] that acetacetic ether absorbs hydrobromic acid forming an unstable hydrobromide. I have found that on passing dry hydrochloric acid gas into pure acetacetic ether (50 grams) cooled to —10° until the gas is no longer absorbed (one and a half hours) that the increase in weight (13.5 grams) corresponds to the formation of a hydrochloride. The theoretical increase would be 14.03 grams. On pouring this mixture into a cold alcoholic solution of sodium ethylate (1 molecule), and then working up as above, about 10 grams of a neutral oil were obtained, two-thirds of which consisted of β-ethoxycrotonic ether (melting-point 30°). A higher-boiling oil containing chlorine was also present.

On allowing 11 grams of acetacetic ether and 22 grams of absolute alcohol to stand at ordinary temperature for one week and then working up as above, 0.5 gram of β-ethoxycrotonic ether (melting-point 30°) were obtained. No better yield was obtained on heating the mixture in a sealed tube at 150°–200°; in this case carbon dioxide was evolved.

These experiments suffice to show clearly that acetacetic

[1] Ann. Chem. (Liebig), **219**, 333. Claisen: Ber. d. chem. Ges., **26**, 2731.
[2] J. prakt. Chem., [2] **47**, 239.

ether with alcohol, alone or in the presence of hydrochloric acid gas, is converted, like a fatty acid or the oxymethylene compounds, into its ester. The reason why the yield is not greater or even quantitative is due to the instability of the ester: it is split very readily by alcoholic hydrochloric acid into acetacetic ether and alcohol. An alcoholic solution of the substance treated with ferric chloride gives at first no color, but very soon (four to five seconds) a deep red coloration sets in, which is due to the formation of acetacetic ether.

Claisen states[1] that he has succeeded in obtaining β-ethoxycrotonic ester from acetacetic ether by means of what he calls "ein eigenthümliches Aethylirungsverfahren." It consists[2] in treating acetacetic ether with orthoformic ether and acetyl chloride. It is now perfectly clear that this is simply an esterfication of acetacetic ether due to the presence of hydrochloric acid and alcohol in the reaction.

The Action of Bromine on β-Ethoxycrotonic Ester.

10 grams β-ethoxycrotonic ester, diluted with an equal volume of absolute ether or of carbon tetrachloride, and cooled to —10°, absorbs bromine (1 molecule) with a great evolution of heat. Hydrobromic acid is noticed after the addition of a few drops of bromine, showing that the di-bromide

$C_2H_5.O\,H$

$CH_3.\dot{C}.\dot{C}.COOR$ does not long exist at this temperature.

$\quad\quad Br\;Br$

This is borne out completely by the further study of the complex reaction. The ethereal solution was allowed to evaporate over sulphuric acid and stick potash *in vacuo*, and the residual oil (16 grams) distilled at reduced pressure: 3 grams were obtained boiling from 110° to 115° at 18 mm.; 7 grams boiling from 125° to 127° at 16 mm.; and 2 grams boiling from 127° to 134° at 16 mm. These oils are all of a neutral or an acid nature, and therefore the acid constituents were removed by shaking in ether solutions with dilute sodium hydroxide at 0°, and the alkaline solution immediately acidified. The neutral portion on distillation *in vacuo*, boiled from 100° to 140° at 18 mm. and is undoubtedly a mixture

[1] Ann. Chem. (Liebig), **277**, 167. [2] Ber. d. chem. Ges., **26**, 2731.

of α- and γ-brom-β-ethoxycrotonic esters, $CH_3.C.(OC_2H_5):CBr.COOR$ and $CH_2Br.C.(OC_2H_5):CH.COOR$.

The acid portion (6 grams) on distillation boiled from 100° to 118° at 16 mm., but the chief portion boiled from 112° to 115°. It behaves precisely like a mixture of α- and γ-bromacetacetic ether. That γ-bromacetacetic ether was present in the mixture was proved by the isolation of the characteristic copper salt by means of copper acetate. It was not possible to isolate the copper salt of α-bromacetacetic ether in a pure state from the above mixture as it is a very unstable compound (see below).

The formation of the above complex mixture on treating β-ethoxycrotonic ester with one molecule of bromine is self-evident from the previous experiments of Nef.[1] The di-bromide of this compound, $\begin{matrix}CH_3.CBr.OC_2H_5\\ H.\dot{C}Br.CO_2C_2H_5\end{matrix}$, does not exist at—10° but splits spontaneously into α-brom-β-ethoxycrotonic ester, $\begin{matrix}CH_3.C.OC_2H_5\\ C_2H_5O_2C.\ddot{C}.Br\end{matrix}$, which, as well as the β-ethoxycrotonic ester, $\begin{matrix}CH_3.C.OC_2H_5\\ H.\ddot{C}.CO_2C_2H_5\end{matrix}$ present at first in excess, is in part split by the hydrobromic acid given off into α-bromacetacetic ether, $\begin{matrix}CH_3.C.OH\\ RO_2C.\ddot{C}.Br\end{matrix}$, and acetacetic ether, $\begin{matrix}CH_3.C.OH\\ H.\ddot{C}.CO_2R\end{matrix}$. On the addition of more bromine this must act on the various substances present, and give rise to the formation of at least four products.

The Action of Bromine on Acetacetic Ether.

Nef has shown,[2] with great precision, that when acetacetic ether is treated with one molecule of bromine, either in ether solution (Duisberg) or in chloroform solution, a mixture of about equal quantities of α-and γ-bromacetacetic ethers is formed. Hantzsch,[3] in view of the experiments of Epprecht,[4] has attempted to throw some doubt on these experiments of Nef. At the present time the facts known are sufficient to ex-

[1] Ann. Chem. (Liebig), **276**, 236; **277**, 76.
[2] Ann. Chem. (Liebig), **266**, 77.
[3] *Ibid.* **278**, 65–69. [4] *Ibid.* **278**, 69.

plain fully the different results obtained by various observers on this subject.

Hantzsch[1] has observed that pure α-bromacetacetic ether goes over on long standing into γ-bromacetacetic ether, and recently he has shown[2] that this change takes place very quickly in the presence of hydrobromic acid.

Nef in his experiments[3] followed the directions of Duisberg: "Nur wurde *sogleich* mit Wasser versetzt und die aetherische Lösung *mit Wasser gewaschen*," etc. It is evident that he thereby removed the α-bromacetacetic ether from the action of the hydrobromic acid, and that other observers, by working less carefully and failing to remove the hydrobromic acid, might thus have converted the α-brom-compound at first present completely into the γ-brom-compound.

It is also noticeable in the original table of Nef[4] that the crude bromacetacetic ether (*i. e.*, well washed and dried, but *not* distilled) gave more diacetosuccinic ether (4 grams from 14 grams oil) on treatment with sodium acetacetic ether than the distilled product of Duisberg (2.3 grams from 13.5 grams oil). This shows that, on distilling, a partial conversion into the γ-product takes place, and by continued distillation it is quite possible that the α-brom-compound is completely destroyed or converted into the γ-product.

In view of the fact that α-and γ-bromacetacetic ethers form copper salts which differ very greatly from one another as regards solubility in most organic solvents, I undertook some additional experiments with Duisberg's bromacetacetic ether in the hope of actually isolating the α- and γ-brom-products through their copper salts, and determining thus the relative amount of each constituent present.

The experiments seemed at first extremely promising. They failed however in the last-named object because of the great instability of the copper salt of α-bromacetacetic ether, and the fact that it is impossible to get a quantitative precipitation of either salt.

The copper salt of α-bromacetacetic ether (the latter prepared by Schönbrodt's method,[5] and boiling from 101°–104° at

[1] Ber. d. chem. Ges., **27**, 355. [2] *Ibid.* 3168.
[3] Ann. Chem. (Liebig), **266**, 80. [4] *Ibid.* 87.
[5] Ann. Chem. (Liebig), **253**, 175.

14 mm. pressure) was prepared by shaking the oil, in the presence of a small quantity of alcohol, with aqueous copper acetate. It comes out, if the proportion of alcohol has been well chosen, as a green, granular precipitate which, after being thoroughly washed with water and 50-per cent. alcohol, and dried *in vacuo*, has no sharp melting-point but decomposes between 125° and 135°, according to the rapidity of heating.[1]

The salt is very unstable if not perfectly pure and dry. It is quite soluble in alcohol, ether, and carbon bisulphide; in chloroform and benzene it is very readily soluble; in ligroin (70°–80°) it is difficultly soluble. The solutions in all except the last solvent are colored a deep grass-green. The alcoholic solution decomposes on standing or on being heated.

It was found that a preparation of Schönbrodts' pure α-bromacetacetic ether, after being kept for ten days in a tightly corked tube, gave with copper-acetate solution a salt which consisted chiefly of copper γ-bromacetacetic ether,[2] showing how very readily this substance is converted into the isomer. The copper salt of γ-bromacetacetic ether can readily be obtained from Duisberg's bromacetacetic ether by shaking it in alcoholic solution with aqueous copper acetate. The following attempt, among many others, was made to prove that Duisberg's bromacetacetic ether is a mixture of the α- and γ-brom-substitution-products: 50 grams of the crude undistilled oil were dissolved in 40 cc. of chloroform and the mixture shaken thoroughly for some time with an excess of aqueous copper acetate; 30 grams of copper salt separated out which, washed with water and cold ether, decomposed and melted at 163°–163.5°. 25 grams of this salt were converted, by means of shaking with dilute sulphuric acid and ether, into the free acid, and 20 grams of the oil obtained. This, on fractional distillation, boiled from 118°–120° at 13 mm. pressure, and was the pure γ-bromacetacetic ether.[3] The copper salt obtained from it has the following properties: It decomposes sharply at 161.5°–162°[4]; it is of a Paris-green color; it is insoluble in ligroin (70°–80°); very difficultly soluble in abso-

[1] Hantzsch gives the point of decomposition at 140°.
[2] *Cf.* Hantzsch: Ber. d. chem. Ges., **27**; 355, 3168.
[3] *Cf.* Epprecht: Ann. Chem. [Liebig], **278**; 77.
[4] Hantzsch [Ber. d. chem. Ges., **27**; 355], gives the point of decomposition as 164°.

lute ether and alcohol; it is moderately soluble in benzene, more readily in chloroform. The solutions are very faintly tinted light green, except the chloroform solution, which is dark grass-green. An analysis gave:

	Found.	Theory.
Cu	13.30	13.19

The dark green chloroform filtrate from the above salt gave on evaporation *in vacuo* 15 grams of oil. This was dissolved in a small quantity of alcohol, and fractionally precipitated by gradual and alternate additions of aqueous copper acetate and alcohol, along with thorough shaking. The first precipitate obtained, after being well washed with water and 50-per cent. alcohol, decomposed between 120° and 138°. The second precipitate obtained decomposed from 128° to 130°. The salts thus obtained when freed from traces of γ-brom isomer by fractional crystallization from ether, resembled *perfectly in solubility and behavior* the copper salt obtained from pure α-bromacetacetic ether.

There can therefore be no question from these experiments of the presence of a considerable amount of α-bromacetacetic ether in Duisberg's "bromacetacetic ether." A sharp determination of the relative amounts of the two constituents present in Duisberg's product could however not be attained, for reasons already given.

This, as above stated, has been determined approximately by the experiments of Nef, who in two ways showed that it is a mixture of about equal parts of α- and γ-bromacetacetic ethers.

ON THE DETERMINATION OF THE AFFINITIES OF ACIDS COLORIMETRICALLY BY MEANS OF POTASSIUM DICHROMATE.

By J. H. Kastle and B. C. Keiser.

It was observed by one of us (Kastle) that the red color of a solution of potassium dichromate could be changed to the yellow color of the normal chromate by the addition of a moderately concentrated solution of sodium acetate. Such being the case, it was thought possible to utilize this reaction

for the determination of the affinities of acids colorimetrically, inasmuch as the reaction is that of the distribution of a base between 2 acids or, what is the same, between an acid and an acid salt; the reaction of the sodium acetate upon the dichromate being represented as follows:

$$2CH_3COONa + K_2CrO_4.CrO_3 + H_2O \rightleftarrows K_2CrO_4 + Na_2CrO_4 + 2CH_3COOH$$

In making the necessary observations it was found impossible to work with equimolecular solutions, for the reason that, not being able to obtain a normal solution of potassium dichromate, owing to its slight solubility, it was found necessary to use a tenth-normal solution of the acetate, and with this solution the changes in color were not sufficiently well marked to be determined by the means at our disposal without exceedingly large experimental errors. Hence it was found necessary, in most instances at least, to use normal solutions of the alkali salts of the several acids with tenth-normal potassium dichromate. The color comparisons were made in narrow glass cylinders, holding 30 cc., similar in shape to Nessler's cylinders, only of thinner glass and more nicely and accurately made. Experiments were made with the normal alkali salts of the following acids: Acetic, formic, butyric, benzoic, crotonic, monobromacetic, etc., the mode of procedure being as follows:

1 cc. of the tenth-normal dichromate is introduced into the measuring-cylinder with 10 cc., or some other suitable quantity, of a normal solution of the sodium or potassium salt of the acid whose affinity is to be determined. In order now to determine the extent of the change in color of the potassium dichromate and thereby the extent of decomposition of the salt, another cylinder, containing 1 cc. of the tenth-normal potassium dichromate is brought, by means of water and tenth-normal caustic soda, to the same dilution and color as the contents of the cylinder containing the tenth-normal dichromate and the salt of the acid. The tenth-normal caustic soda is of course added drop by drop, comparison being made between the two cylinders after the addition of each drop, until the two are as nearly alike in tint as possible. It should be said in this connection that, even by this rough

method of color-comparison, it is quite possible easily to detect differences in color caused by one drop of the tenth-normal solution of caustic soda even when the colors are almost of the same shade and tint. It is really astonishing to observe what minute differences in color can be distinguished between the yellow of the chromates and the red of the dichromates. The results obtained with the salts of the several acids employed are given below in Table I. 1 cc. of tenth-normal potassium dichromate was used in each experiment.

TABLE I.

No. of expt.	Sodium salt used.	Cc. of the N. sol. of salt used.	Cc. 0.1 N. NaOH required to produce same color with $K_2Cr_2O_7$ as salt.	Quantity of salt decomposed in grams.	Percentage decomposition.	Affinity.
1	Acetate	5	1.2	0.0090	2.19	44.0
2	"	10	1.5	0.0123	1.5	65.6
3	"	15	1.65	0.0135	1.09	90.7
4	"	20	1.7	0.0139	0.84	116.0
5	"	7	1.3	0.0106	1.85	53.0
6	Formate	10	0.65	0.0044	0.64	153
7	"	20	1.00	0.0068	0.5	199
8	"	30	1.1	0.0075	0.36	272
9	Butyrate	1	0.8	0.0064	6.4	11.5
10	"	2	1.2	0.0120	6.0	16.0
11	"	3	1.3	0.0130	4.33	22.1
12	"	5	1.6	0.0160	3.2	30.2
13	"	7	1.75	0.0175	2.5	39.0
14	Benzoate	10	0.8	0.0115	0.8	124
15	Brom-acetate	20	0.3	0.00483	0.15	665
16	"	10	0.25	0.00402	0.25	339
17	Crotonate	5	0.95	0.0102	1.8	51.6
18	"	10	1.3	0.0140	1.3	74.6
19	"	15	1.45	0.0152	0.93	102.0
20	"	20	1.55	0.0162	0.75	128.0

The percentage-decomposition of the salt of the acid whose affinity is to be determined, is calculated as follows: In experiment 1, for example, the alteration in color produced by 5 cc. normal sodium acetate was also brought about by 1.2 cc. tenth-normal caustic soda; hence in view of the action taking place

$K_2CrO_4.CrO_3 + H_2O + 2NaCH_3CO_2 = K_2CrO_4 + Na_2CrO_4 + 2CH_3COOH$ and

$K_2CrO_4.CrO_3 + 2NaOH = K_2CrO_4 + Na_2CrO_4 + H_2O$ —

we have:

$$2NaOH : 2CH_3COONa = 0.0048 : x.$$

$x = 0.0090$ = the quantity of sodium acetate decomposed. Comparing this with the quantity of acetate started with we obtain the percentage-decomposition; and, knowing the percentage-decomposition and, for the purposes of comparison, making the affinity of potassium dichromate equal to 1, the affinity of acetic acid, under the conditions of the above experiment, is equal to $1 \times \frac{100 - 2.19}{2.19} = 44$. This signifies that, at the dilution of the experiment and acting according to the relative masses of the two substances, the acetic acid is forty-four times as strong as potassium dichromate. In the same way the other members in the last two columns are obtained. If now we compare the numbers obtained for the several acids at corresponding dilutions, it is seen that these members bear to each other the same relation as do the numbers obtained by other observers for the affinities of these acids. The following arrangement brings out this relation very clearly:

Acid.	With 5 cc. N. sol.	7 cc.	10 cc.	15 cc.	20 cc.
Acetic	44	53	65.6	90.7	116
Formic	....	....	153.	....	199
Butyric	30.2	39	....	....	....
Benzoic	....	....	124	....	....
Crotonic	51.6	....	74.6	102.0	128
Monobromacetic	....	....	399.	....	665

An examination of these results reveals, further, that essentially the same relation exists between the numbers obtained for one quantity of the several salts used, and those obtained for other quantities. For example, the number found for crotonic acid, using 10 cc. of the normal solution of its sodium salt, is 74.6; for 5 cc. of the acetate and crotonate used, however, the numbers for acetic and crotonic acids are, respectively, 44 and 51.6. Hence by proportion, calculating upon the basis of the number found for acetic acid, where 10 cc. of sodium acetate are used—which is 65.6—we should obtain 76

as representing the strength of crotonic acid as compared with that of acetic, 65.6; thus

$$44 : 51.6 :: 65.6 : x;\ x = 76-$$

whereas the last term as determined experimentally is, as stated above, 74.6.

This signifies that the relative strength of these two acids is the same for a large as well as a small quantity of their salts used. In the same way the several values of crotonic acid as compared with acetic are as follows:

	x Calculated for crotonic acid.	x Found.
$44 : 51.6 = 65.6 : x;$	76	74.6
$44 : 51\ 6 = 90.7 : x;$	106	102.0
$65.6 : 74.6 = 116 : x;$	131	128.0

In the same manner the following values are obtained for butyric, bromacetic, and formic acids:

	x Calculated for butyric acid.	x Found.
$44 : 30.2 = 53 : x;$	36.4	39.0
	x Calculated for bromacetic acid.	x Found.
$65.6 : 399 = 116 : x;$	705	665
	x Calculated for formic acid.	x Found.
$65.6 : 153 = 116 : x;$	270	199

Except in the case of formic acid the differences in the results calculated and observed, come within the limit of the experimental error of the method employed for the color-measurement, and further, a comparison of the results obtained by this method with those of other methods for the determination of the affinities of acids, shows conclusively that this method affords a means of determining the relative strengths of certain of the monobasic acids. For the purpose of making such a comparison some of the numbers for the acids here employed are given along with those obtained by this method:

	I.	II.	III.	IV.
Acetic	1.23	0.43	0.35	65.6
Formic	3.9	1.68	1.31	153.0
Butyric	0.98	0.32	0.30	47.0
Benzoic[1]	....	....	....	124.0
Crotonic[2]	....	....	....	74.6
Monochloracetic, and	7	4.90	4.3	....
hence, monobromacetic	7 [about]	4.90 [about]	4.3 [about]	3.99

[1] Formic acid is stronger than benzoic. For crotonic and benzoic acids see the numbers given in the article "Affinity"—Watts' Dictionary [New Edition].

[2] At certain dilutions acetic acid seems stronger than crotonic, whereas at others the reverse is true. These two acids have very nearly the same strength.

The numbers in column I in the above table were obtained by Ostwald by determining the distribution of a base between two acids; in II, by the method of electrical conductivities; in III, by the saponification of methyl acetate; in IV, by the colorimetric method herein described.

It will be observed that by means of the colorimetric method it is certainly possible to arrange these acids in the order of their strength; and in most cases the agreement between this and other methods is as close as could be expected of methods so entirely different. It is not claimed for the new method that it is as extensive or far-reaching or accurate as any of the methods now in general use. In the case of very strong acids, for example, whose salts it is impossible for the potassium dichromate to decompose, no exact results can be obtained. For example, 20 cc. of a 3 N. solution of potassium chloride was added to 1 cc. tenth-normal potassium dichromate without causing any appreciable change of color. Hence all that could be learned in cases of this kind would be that the acid was very strong as compared with acetic. With colored acids also it is obvious that no results could be obtained by this method. With dibasic acids also the results might be uncertain owing to the formation of acid salts; in fact certain results already obtained with a few of the commoner dibasic acids indicate that the numbers obtained for these acids are too low. The few monobasic hydroxy acids tried, lactic, salicylic, etc., gave unsatisfactory results, or perhaps it would be more in keeping with the facts to say that they gave no results at all, in that the color of the potassium dichromate remained unchanged after the addition of considerable quantities of a lactate or a salicylate. It is quite possible however, that the hydroxy portion of these acids is as strong or stronger than the potassium dichromate in which case there would be no change of color. It would thus appear that the relative strengths of a great many acids cannot be determined by the new method; nevertheless in consequence of its beauty and simplicity it is certainly not without interest. Even though applicable in comparatively few cases, it can doubtless be applied to all weak or moderately strong acids whose number is by no means inconsiderable. It possesses the further advantage that it can

be applied to the determination of the affinities of rather insoluble acids such as benzoic acid, etc., in concentrated solution, for the reason that ofttimes the more insoluble the acid the more soluble its alkaline salts. It is our purpose to test this method upon all classes of acids as soon as possible—making use of a colorimeter to insure the accuracy of the color-comparisons. Inasmuch, however, as the work cannot be done immediately, it is deemed advisable to submit the results already obtained as preliminary to a more extended investigation, believing that they are not altogether wanting in importance or interest.

STATE COLLEGE OF KENTUCKY, April, 1895.

Contribution from the Sheffield Laboratory of Yale University.

ON SOME AZO AND AZIMIDO COMPOUNDS.

BY W. G. MIXTER.

Benzoyl Metazoparatoluide.—Pure benzoyl *m*-nitro-*p*-toluide,[1] dissolved in alcohol, was subjected to the reducing action of zinc and ammonia until there was no further separation of the azo compound from the solution. The precipitate was washed with alcohol, digested with dilute hydrochloric acid to remove zinc, then washed with water, dried, and finally crystallized from glacial acetic acid. The yield was 50 per cent. of the nitrotoluide taken. The following is the analysis:

	C.	H.	N.
Calculated for $C_{28}H_{24}N_4O_2$	75.0	5.35	12.50
Found	75.17	5.50	12.71

Benzoyl metazoparatoluide, $[C_6H_3.(1)CH_3.(4)NHC_7H_4O.(5)N]_2$, is almost insoluble in alcohol, is sparingly soluble in boiling glacial acetic acid, from which it separates in orange-colored fibres as the solution cools. It melts at 242°. It yielded only an impure, tarry product when treated with alkalies or sulphuric acid to remove the benzoyl group.

Acetyl Metazoorthotoluide.—The acetyl *m*-nitro-*o*-toluide

[1] The nitro compound was prepared by adding crystallized benzoyl *p*-toluide to 10 parts of nitric acid having a density of 1.4. The mixture without warming was shaken for a time and then poured into water. The product, after crystallizing from alcohol, melted at 145°.

used was made by Mr. G. F. Campbell, who did not have time to finish the investigation commenced with it. He nitrated *o*-acettoluide at the ordinary temperature with nitric acid of density 1.4. The product, crystallized from alcohol, melted at 202°. Beilstein and Kuhlberg[2] give the melting-point of 197° for the compound. The reduction was made in alcohol with zinc and ammonia. The azo compound separated slowly. It was washed with alcohol, hydrochloric acid, and water, and then dissolved in boiling glacial acetic acid. The solution, on cooling, yielded orange-colored fibres of the azo compound.

	C.	H.	N.
Calculated for $C_{18}H_{20}N_4O_2$	66.67	6.17	17.28
Found	66.62	6.17	17.24

Acetyl metazoorthotoluide, $[C_6H_3.(1)CH_3.(2)NHC_2H_3O.(5)N]_2$, does not melt at 310°, is almost insoluble in alcohol, and not very soluble in hot glacial acetic acid. Attempts to obtain pure *m*-azo-*o*-toluidine were not successful. The azotoluide was not decomposed by hydrochloric acid. It was therefore dissolved in warm sulphuric acid, the solution poured into water, and ammonia added. The precipitate which formed was washed with water and crystallized from alcohol in which it was very soluble. The product was dark red, melted at 199°, and yielded 21.88 per cent. of nitrogen, azotoluidine having 23.33 per cent. It formed deep red solutions with sulphuric and hydrochloric acids. Hydrogen platinic chloride gave in an aqueous solution of the chloride a bulky precipitate which, after washing and drying, was found to contain 2 per cent. less platinum than was calculated for the platinum salt of azotoluidine.

Benzoyl Azoxylide.—The benzoyl nitroxylide used in the investigation was made as follows: Benzoyl xylide from commercial xylidine and benzoyl chloride was added to nitric acid of density 1.4 and, when the temperature rose to 25° or 30°, the mixture was poured into water. By repeated crystallization from alcohol benzoyl nitroxylide melting at 187° was separated from products with lower melting-points. It yielded when saponified with sulphuric acid nitroxylidine,

[2] Ann. Chem. (Liebig), **158**, 345.

$C_6H_3.(1)CH_3.(3)CH_3.(4)NH_2.(5)NO_2$, melting at 73°. The benzoyl nitroxylide was reduced in an alcoholic solution by zinc and ammonia, and the precipitate which separated was purified by washing and then dissolved in hot glacial acetic acid. The compound separated in orange-colored fibres as the solution cooled.

	C.	H.	N.
Calculated for $C_{30}H_{28}N_4O_2$	75.63	5.88	11.77
Found	75.42	5.83	11.85

Benzoyl azoxylide, $[C_6H_2.(1)CH_3.(3)CH_3.(4)NHC_7H_5O.(5)N_2]$, is slightly soluble in hot alcohol, and decomposes without melting at 280°–290°.

In the preparation described of the azo derivatives of toluidine and xylidine there separated from the alcoholic solution in which the reduction was made, no azoxy compound—which is the first product that may be formed when a nitro compound is reduced. This was doubtless due to the solubility of the azoxy compounds, since if they were formed and did not separate they would have been reduced to azo compounds. This view of the solubility of the azoxy compounds in question is supported by the observations of Bankiewicz[1] who found the acetyl-*m*-azoxy-*p*-toluide (acetamidoazoxytoluene) to be soluble in alcohol and the corresponding azo compound to be insoluble. The former he made by reducing acetyl nitrotoluide with ammonium sulphide and the latter with sodium amalgam in an acetic-acid solution. Mr. G. F. Campbell, of this laboratory, obtained acetyl-*m*-azo-*p*-toluide by reduction with zinc and ammonia, which was insoluble in alcohol and otherwise resembled Bankiewicz's compound. The acetyl and benzoyl derivatives of ortho-, meta-, and para-azoxyaniline,[2] I found to be insoluble, or nearly so, in alcohol. They separate when the nitro compounds from which they are made are reduced in alcoholic solution. The same is true of benzoyl *o*-azoxy-*p*-toluide,[2] but this is the only known insoluble homologue of benzoyl azoxyanilide or acetyl azoxyanilide. Acetyl azoanilide is soluble in alcohol, while

[1] Ber. d. chem. Ges., **22**, 1396. [2] This Journal, **5**, 1, 282.

the homologues of it thus far obtained are insoluble. It is impossible as yet to make a rule regarding the solubility of the compounds in question, but this much appears to be indicated: If in benzoyl azoxyanilide or acetyl azoxyanilide one or more atoms of hydrogen of the benzene group is replaced by a radicle, the resulting compound is likely to be soluble in alcohol, while an insoluble compound results by a similar replacement in benzoyl azoanilide or acetyl azoanilide.

Benzoylazimidotoluene.—Azimidotolual was first obtained by Ladenburg,[1] who called it amidoazotoluylen. Boessneck[2] decribed the acetyl derivative, which was later obtained in two modifications by Zincke and Lawson,[3] who prepared a number of derivatives of azimidotoluene. The benzoyl derivative is easy to prepare because of its stability and insolubility in water and dilute acids. In one experiment 7 grams of benzoyltoluidenediamine, made from benzoyl *m*-nitro-*p*-toluide, were dissolved in hot water containing 15 cc. of hydrochloric acid, and the solution was diluted to 2 liters to keep the diamine in solution when cool. Nitrous fumes were then passed into the solution, causing at once a turbidity. When the separation of the benzoylazimidotoluene was completed it was filtered off, washed and dried. The product weighed 6.4 grams. A more convenient way, which was used several times, is to add potassium nitrite to an acid solution of the diamine. Benzoylazimidotoluene dissolves easily in alcohol, from which it separates on evaporation of the solution in white fibres, melting at 125°. The following is the analysis:

	C	H	N
Calculated for $C_{14}H_{11}N_3O$ ...	70.89	4.64	17.72
Found	70.40	4.97	17.76

Benzoylazimidotoluene, $C_6H_3.(1)CH_3.(4)N{:}N.(5)N.C_7H_5O$ decomposes slightly after a time, as is apparent from the odor of benzoic acid, and is readily saponified by acids and alkalies, including ammonia. When heated with aniline, benzoyl anilide is formed; with phenylhydrazine, benzoylhydrazine results.

[1] Ber. d. chem. Ges., **9**, 220. [2] *Ibid.* **19**, 1758.
[3] Ann. Chem. (Liebig), **240**, 110.

Azimidoxylene.—Benzoyldiamidoxylene, $C_6H_3.(1)CH_3.(3)CH_3.(4)NHC_7H_5O.(5)NH$, was dissolved in warm dilute hydrochloric acid, and after the solution had cooled potassium nitrite was added. A portion of the azimido compound formed separated and a part remained in the solution from which it was precipitated by neutralizing the acid present with ammonia. The product, after crystallizing from alcohol, melted at 111° and gave 16.79 per cent. of nitrogen, theory requiring 16.73 in benzoylazimidoxylene, $C_6H_3.(1)CH_3.(3)CH_3.(4.5)N_3.C_7H_5O$.

One gram of another preparation of benzoylazimidoxylene was treated with hot concentrated hydrochloric acid and water was added. The solution, on cooling, deposited benzoic acid, which was filtered off and to the filtrate ammonia was added in slight excess. Azimidoxylene separated as a white powder, which was easily washed. After drying over sulphuric acid it melted at 196°. It was, however, not quite pure, as it yielded only 27.46 per cent. of nitrogen, against 28.56 required by the formula $C_6H_3.CH_3.CH_3.N_3H$. Another preparation, which melted at 186°, gave 28.28 per cent. of nitrogen.

Azimidoxylene is slightly soluble in cold water, more soluble in hot water, from which it is deposited on cooling as a white meal. It is soluble in alcohol, in ether, in nitric acid, and in hydrochloric acid. The hydrochloric-acid solution does not give a precipitate with hydrogen platinic chloride. Azimidoxylene is soluble in an excess of ammonia and separates when the ammonia is boiled off. Its acid character is also shown by its forming a silver salt. To a solution of it in nitric acid silver nitrate was added; a white curd precipitated which, after washing and drying, yielded 36.79 per cent. of silver; calculated for $C_6H_3.CH_3.CH_3.N_3.Ag$, 42.93 per cent. In another attempt to obtain the silver salt pure, an alcoholic solution of silver nitrate was added to an alcoholic solution of azimidoxylene. A very bulky gelatinous precipitate formed, which was washed with water and dried at 100°. It was permanent in light. Silver was found in it to the extent of 44.8 per cent. The excess over the theoretical amount of silver is doubtless due to the difficulty in washing the salt.

Contributions from the Chemical Laboratory of the Lehigh University.

II—ON THE ACTION OF CERTAIN ALCOHOLS WITH METADIAZOBENZENESULPHONIC ACID.[1]

By W. B. Shober and H. E. Kiefer.

One of us several years ago investigated the action of methyl, ethyl, and propyl alcohols upon paradiazobenzenesulphonic acid.[2] As a result of that investigation it was found that, when the decomposition of the diazo compound was effected with methyl alcohol at diminished pressure, the course of the action was such as to give rise to the formation of the hydrogen compound only, benzenesulphonic acid; at ordinary and slightly increased pressures both benzenesulphonic acid and methoxybenzenesulphonic acid were formed, thus showing that the hydrogen- and alkoxy-reactions had both taken place.

When the diazo compound and the alcohol were heated in a sealed tube only the methoxy product was formed. When ethyl and propyl alcohols were used, the hydrogen product alone was formed. In view of these results and others which are recorded, it was desirable to determine the action of these same alcohols upon *meta*-diazobenzenesulphonic acid. The starting-point in this work was the preparation of metanitrobenzenesulphonic acid. Of the several methods given the one of Laurent[3] was selected.

Pure benzene was converted into benzenesulphonic acid and this was treated with fuming nitric acid, giving rise to the formation of the three isomeric nitrobenzenesulphonic acids. After standing, the mass was poured into a large quantity of water. During this preparation it was found necessary to use nitric acid not stronger than that having a specific gravity of 1.5, and to keep the temperature low by continually plunging the flask into running water. In one

[1] From the thesis of H. E. Kiefer, submitted to the Faculty of the Lehigh University for the degree of Master of Science, June, 1894.

[2] This Journal, **15**, 379.

[3] Jsb. Chem., 1850, 418.

case in which we used acid of specific gravity 1.6 and allowed the temperature to rise, almost the entire amount of benzene originally used was converted into metadinitrobenzene. The water solution was then neutralized with barium carbonate, filtered, and concentrated.

An attempt was made to separate the three barium salts by crystallization, as advised by Limpricht. The result was not satisfactory. The experiment was repeated. After removing the nitrobenzenes the acids were neutralized with pure barium carbonate. Repeated attempts to obtain good crystals failed. The barium salts were then converted into the potassium salts, these into the chlorides, and finally into the amides. The amides were separated by fractional crystallization. Each lot of crystals was repeatedly crystallized until a sharp melting-point was obtained. The metanitrobenzenesulphonamide melts at 161°, the para compound at 131°, and the ortho compound at 186°. There was no difficulty in making the separation in this manner. The meta amide was divided into 12–15 gram portions. Each portion with about an equal weight of concentrated hydrochloric acid was heated in a sealed tube for ten hours at a temperature of 150°.[1] The contents of the tube were then evaporated to dryness and the ammonium salt of metanitrobenzenesulphonic acid thus obtained, was recrystallized until it appeared in long colorless prisms. The crystals were dissolved in water strongly ammoniacal, and sulphuretted hydrogen passed into the solution until there was no further rise in the temperature of the mass. After removing the excess of ammonium sulphide and sulphur, the solution was acidified with hydrochloric acid and allowed to stand twelve hours, when the amido acid separated out in flat, white, flaky crystals. It crystallizes also in fine needle-like forms.

This metamidobenzenesulphonic acid was converted into the diazo compound by mixing the acid with a very small quantity of water and passing a rapid current of cooled nitrous fumes through the mass. When the mixture became

[1] In one experiment four tubes were placed in the furnace at the same time. At the end of eight hours one of them was partially filled with a very black liquid, which upon investigation was found to have the properties of a dye. Repeated attempts to obtain this substance again have failed.

clear, due to the solution of the diazo compound in the water, cooled alcohol was added, and it was allowed to stand in a freezing-mixture until the fine, yellowish needles of the diazo compound separated out. We found the compound to be very explosive, thus confirming Berndsen's observations,[1] although Meyer and Stüber[2] state that the compound is not explosive. As Berndsen has pointed out they were probably working with a mixture of the diazo compound and the amido acid which had escaped the diazotisation.

Action of Methyl Alcohol on Metadiazobenzenesulphonic Acid under Diminished Pressure.—About 7 grams of the diazo compound and 100 cc. of dehydrated methyl alcohol were placed in a flask.[3] The contents of the flask were heated to boiling on a water-bath for two and a quarter hours. At this point the suction was shut off, and the experiment could not be completed. When it was resumed after an interval of thirty-six hours, the decomposition was complete in a few minutes. During the experiment the pressure varied from 360 to 410 mm. of mercury (absolute pressure). The alcohol changed color until it was a deep amber tint. The solution was filtered, the alcohol distilled off, and the residue, after dilution with water, was neutralized with barium carbonate. The barium salt was converted into the potassium salt and this into the amide. Upon crystallizing, two amides were found, one of them separating out in long slender needles, the melting-point of which was found to be 128°. This substance is shown by the analysis given below to be methoxybenzenesulphonamide—presumably the meta modification, which we believe has not been described before. The other amide had a melting-point of 152°. From this fact and the conditions under which it was formed, it was concluded that the compound was benzenesulphonamide. These two amides were separated by mechanical means, and it was found that the methoxy amide had been formed in larger quantity than the hydrogen amide.

Action of Methyl Alcohol on Metadiazobenzenesulphonic Acid at Ordinary Pressure.—7.5 grams of the diazo compound and

[1] Ann. Chem. (Liebig), **177**, 88. [2] *Ibid.* **165**, 165.
[3] For description of the apparatus see this Journal, **15**, 324.

150 cc. of methyl alcohol were placed in a flask to which was attached a reflux condenser. The mixture was boiled on a water-bath; at the expiration of thirty minutes the decomposition was complete, the solution being a bright amber color. The decomposition-products were treated as before. Two amides were obtained, the methoxy compound being present in much larger quantity than the hydrogen compound.

Action of Methyl Alcohol on Metadiazobenzenesulphonic Acid at 400 mm. Pressure.—5 grams of the diazo compound and 100 cc. methyl alcohol were placed in a pressure-flask[1] and heated. The reaction took place rapidly, the decomposition being complete in *seven* minutes. The resulting residue was converted into the amide as above. Upon crystallizing, two kinds of crystals were found, the melting-point of one being 128°, that of the other 152°—thus indicating that both reactions had taken place.

Action of Methyl Alcohol on Metadiazobenzenesulphonic Acid at 800 mm. Pressure.—6 grams of the diazo compound and 120 cc. methyl alcohol were heated on a water-bath at a pressure of 800 mm. mercury. The reaction was complete in ten minutes, the solution being a faint amber color. The products of decomposition were treated as before. Two amides were again found, the methoxy amide being present in great excess.

The methoxy compound was analyzed with the following results:

0.2024 gram substance gave 0.2156 gram $BaSO_4$ (Carius' method).

0.200 gram substance gave 0.3281 gram CO_2 and 0.0085 gram H_2O.

	Mol. wt.	Calculated for $C_7H_9SNO_3$.	Found.
C_7	83.79	44.89	44.74
H_9	9.00	4.82	4.92
S	31.98	17.13	17.08
N	14.01	7.51	....
O_3	47.88	25.61	....
	186.66	100.00	

[1] For description of apparatus, see this Journal, **15**, 106.

Action of Ethyl Alcohol on Metadiazobenzenesulphonic Acid at Ordinary Pressure. — Berndsen[1] states that when metadiazobenzenesulphonic acid is boiled with absolute alcohol at the ordinary pressure, no action takes place. We cannot confirm this statement. Our first experiment was conducted as follows: 8 grams of the diazo compound prepared as described above, and 160 cc. of absolute alcohol[2] were placed in a flask to which was attached a reflux condenser. The flask was heated slowly; the *reaction began almost immediately*, and in *seven* minutes the decomposition was complete, leaving a clear solution of deep amber color. The experiment was repeated later with precisely the same results. The products of the decomposition were examined, as in the other cases, by converting the residue into the amides. Two kinds of crystals were found: one melting at 126°, which is shown by the analysis below to be ethoxybenzenesulphonamide; the other, melting at 149°, is benzenesulphonamide. The ethoxybenzenesulphonamide, presumably the *meta* modification, not having been described before was analyzed with the following results:

0.1878 gram substance gave 0.2194 gram $BaSO_4$ (Carius' method).

0.5 gram substance gave 0.3595 gram N (Kjeldahl-Gunning method).

	Mol. wt.	Calculated for $C_8H_{11}SNO_3$.	Found.
C_8	95.76	47.72	....
H_{11}	11.00	5.48	....
S	31.98	15.94	16.04
N	14.01	6.98	7.19
O_3	47.88	23.88	....
	200.63	100.00	

Berndsen's inability to effect the decomposition of the diazo compound with absolute alcohol at ordinary pressure was probably due to the fact that the compound with which he worked was metamidobenzenesulphonic acid which had escaped diazotisation, and not metadiazobenzenesulphonic acid.

[1] Ann. Chem. (Liebig), **177**, 89.

[2] The alcohol had been allowed to stand over lime and afterwards over anhydrous copper sulphate for about two weeks.

Action of Ethyl Alcohol on Metadiazobenzenesulphonic Acid at 400 mm. Pressure.—11 grams of the diazo compound and 200 cc. absolute ethyl alcohol were placed in a flask and treated as before. The reaction was energetic, the decomposition being complete in less than five minutes. Examination of the product revealed the presence of two different amides, one melting at 126° and the other at 150°.

Berndsen[1] decomposed the same diazo compound with absolute alcohol at the same pressure, but was unable to separate the two substances, and consequently unable to obtain the benzenesulphonamide in a pure condition. He says: "Dieses Sulfobenzolamid krystallisirte aus heissem Wasser in kleinen Nadeln oder Blättchen, aus Alkohol und Aether in kleinen sechsseitigen Prismen, *die aber noch durch eine klebrige Substanz verunreinigt waren* . . Aber die Schwankungen im Schmelzpunkte zeigten, das kein reines Sulfobenzolamid vorlag, das bei 149° schmelzen soll, während verschiedene Krystallisationen meiner Verbindung bei Temperaturen schmolzen, die zwischen 139° und 159° lagen." The substance with which Berndsen worked was undoubtedly a mixture of ethoxybenzenesulphonamide and benzenesulphonamide.

Action of Ethyl Alcohol on Metadiazobenzenesulphonic Acid at 800 mm. Pressure.—8 grams of the diazo compound and 160 cc. absolute alcohol were placed in the pressure-flask and heated rapidly until the manometer indicated a pressure of 800–820 mm. mercury. The action began almost immediately upon applying heat and was complete in less than five minutes. Upon converting the decomposition-products into the amides, it was found that both the ethoxy- and hydrogen-reactions had taken place. The hydrogen compound was present in very small quantity.

Action of Ethyl Alcohol on Metadiazobenzenesulphonic Acid at Diminished Pressure.—7 grams of the diazo compound and 145 cc. of absolute alcohol were placed in a flask on a water-bath and heated, the pressure being 440 mm. (absolute pressure). The reaction was complete in less than twenty minutes. The decomposition-products were treated as before. *Two* amides were found.

[1] Ann. Chem. (Liebig), 177, 91.

Action of Propyl Alcohol on Metadiazobenzenesulphonic Acid at an Increased Pressure.—6 grams of the diazo compound and 125 cc. of propyl alcohol which had been dehydrated over lime, filtered, and distilled, were placed in the pressure-flask and heated as rapidly as possible. Decomposition began at once. The pressure increased rapidly; when the manometer indicated 800 mm., the decomposition was complete. Length of time, seven minutes.

The decomposition in this case was more complicated than with the lower alcohols. The resulting liquid had a dirty-brown appearance, and the yield of the principal products was very much smaller. The residue was treated as in the other cases. Owing to the small quantity of amide obtained it was impossible to decide whether or not both reactions had taken place. A sufficient quantity of an amide was obtained however, to show that it had a melting-point of 122°, and to make a sulphur determination:

0.158 gram of the substance gave 0.170 gram $BaSO_4$ (Carius' method), corresponding to 14.78 per cent. of sulphur. The theory for propoxybenzenesulphonamide requires 14.90 per cent. of sulphur.

Action of Propyl Alcohol on Metadiazobenzenesulphonic Acid at Ordinary Pressure.—5 grams of the diazo compound and 100 cc. propyl alcohol were placed in a flask to which was attached a reflux condenser, and heated. The decomposition was complete in fifteen minutes. The products were treated as before. Upon crystallizing the amides, two were found, one melting at 122° and the other at 150°; the latter was present in very small quantity.

Summary.

I. Methyl alcohol at various pressures gives *both* reactions. At the highest pressures the methoxy compound is formed in greatest excess.

II. Ethyl alcohol gives similar results.

III. Propyl alcohol at ordinary pressures gives both reactions.

Comparing these results with those obtained by the decom-

position of *para*diazobenzenesulphonic acid,[1] with the same alcohols under essentially the same conditions, we find that the *para* compound when decomposed with :

I. Methyl alcohol at reduced pressure gives *only* the hydrogen reaction.

II. At other pressures the para and meta compounds give similar results.

III. Ethyl alcohol gives *only* the hydrogen reaction.

IV. Propyl alcohol gives *only* the hydrogen reaction.

The metadiazo compound is decomposed with much greater ease than the para compound, the latter requiring with various alcohols at various pressures from two to eight hours, while with the former but a few minutes were usually required.

REPORT.

The Molecular Complexity of Liquids.

The study of the physical properties of substances in the form of vapor has resulted in the perfection of several methods for the determination of their molecular weights in that condition. Since it has been found, too, that the condition of a substance in dilute solution is at least nearly identical with that of the same substance in the form of vapor at the same temperature and pressure, examination of the behavior of such solutions has led to the perfecting of methods of molecular-weight determination for substances for which vapor-density methods were not readily available. All the results obtained, however, have had to do with substances in a state of vapor only, or in a condition practically identical with the gaseous state; the complexity of the molecules of liquids was unknown and no suitable method for its determination has, until recently, been proposed. It is intended in this short review to call attention to the results obtained in this field of research chiefly by Prof. W. Ramsay, of London.

Eötvös, in 1886,[2] had called attention to the fact that the rate of change of the surface-energy of a liquid with respect to the temperature is an approximately constant one, or, in other words, $\frac{d\gamma s}{dt} = k$, where γ = surface-tension, s = surface, and t =

[1] *Loc. cit.* [2] Ann. der Phys. Wied., **27**, 448 (1886).

temperature measured downward from the critical temperature. The reasoning upon which Eötoös based his deductions from experimental results was, however, at fault.[1] One suggestion that he made has nevertheless proved of great value: in order to make his formula apply to all liquids he makes s = the molecular surface, *i. e.*, that surface over which, whatever the liquid, the same number of molecules are distributed. He assumes that this surface $= (Mv)^{\frac{2}{3}}$, where Mv = the molecular volume of the liquid in question under the conditions of the experiment, *i. e.*, that volume which, whatever the liquid, contains the same number of molecules. If we imagine this volume a cube, then any edge would be represented by $(Mv)^{\frac{1}{3}}$, and any face by $(Mv)^{\frac{2}{3}}$. Assuming this value for s, Eötvös' formula becomes $\gamma(Mv)^{\frac{2}{3}} = k(T - T')$, where T is the critical temperature and T' that of the experiment.

Ostwald,[2] in his *Lehrbuch*, commenting upon the work of of Eötvös, expresses the hope that this colligative property of liquids may serve for the determination of the molecular weights of substances in the liquid state.

The first paper by Ramsay and Shields[3] describes an elaborate series of experiments undertaken in the hope of establishing the existence of a law connecting the critical temperature of a liquid and some one of the properties peculiar to the liquid state, in the same way that the volume-energy law of gases, $pv = RT$, connects the absolute temperature and the volume of a gas.

In the formula $pv = RT$, if v be constant, p decreases with T; when $p = 0$, $T = -273°$. Therefore, the origin of the scale of temperature is the origin of the scale of pressure. Correspondingly, in Eötvös' formula $\gamma s = K\tau$ (where τ is used to represent $T - T'$ or the number of degrees below the critical temperature at which the experiment is conducted), if s be constant, γ decreases with τ until $\gamma = 0$ when $\tau = 0$, or when the critical temperature is reached. Therefore, the origin of the scale of temperature is the origin of the scale of tension. Assuming, therefore, with Eötvös, that the molecular surface s may be regarded as equal to the molecular volume, Mv, raised to the two-thirds power, they have tested the formula $\gamma (Mv)^{\frac{2}{3}} = K\tau$ by making determinations of the rise of liquids in capillary tubes at temperatures ranging from $-89.8°$ to the critical temperatures of the liquids.

The liquids examined were ether, methyl alcohol, ethyl

[1] Ramsay and Shields: Phil. Trans. **184**, A, 660, (1893).

[2] 2nd. Ed., pp. 1129 and 1130.

[3] Phil. Trans. **184**, A, 647, (1893); also Ztschr. phys. Chem., **12**, 433, (1893).

alcohol, methyl formate, ethyl acetate, carbon tetrachloride, benzene, chlorbenzene, and acetic acid. The data made use of were for the most part those determined by Ramsay and Young.[1]

The apparatus consisted essentially of a capillary tube whose bore was accurately known at a certain point at which the level of the liquid within was always made to stand, enclosed in a sealed glass tube of large bore which contained nothing except the pure liquid and its vapor. The differences between the levels in the capillary and in the outer tube were measured by means of a cathetometer; correction being made at the same time for the capillary rise in the outer tube. The apparatus was so arranged that the level in the capillary always stood at the same point when measurements were being made; this avoided errors due to the varying size of the capillary tube. The outer tube was surrounded by a jacket filled with the vapor of some pure liquid whose boiling-points under various pressures were accurately known; by means of a mercury-gauge, the pressure under which the liquid boiled could be varied so as to obtain any desired temperature for the jacket. With this apparatus, experiments were made for each of the nine liquids mentioned, at intervals of 10° for the most part, from 20° to the critical temperarure. In the case of ether, methyl formate, and ethyl acetate, experiments were also made at −89.8°, the tube being surrounded with boiling nitrous oxide.[2]

The results show that the formula $\gamma(Mv)^{\frac{1}{3}} = K\tau$ does not express the truth, but that for ether, methyl formate, ethyl acetate, carbon tetrachloride, benzene, and chlorbenzene, the formula $\gamma(Mv)^{\frac{1}{3}} = K(\tau - d)$, where d is a small number—averaging about 5°,— expresses with accuracy the variation of the surface-energy with the temperature to within 20°–30° of the critical temperature. Thus, in a drawing where the ordinates represent temperatures, and the abscissæ surface-energies, the "curve" representing the change of surface-energy with temperature is a straight line to within a few degrees of the critical temperature. The surface-tension was calculated by means of the formula $\gamma = \frac{1}{2}rhg(\rho - \sigma)$, where r = radius of capillary tube, h = capillary rise, g = gravitation-constant, ρ = density of the liquid at the temperature of

[1] For ether, methyl alcohol, and ethyl alcohol, see Ramsay, and Young: Phil. Trans., **178**, A, 57, 313, (1887); **177**, A, 123, (1886). For methyl formate, and ethyl acetate, see Young and Thomas: J. Chem. Soc. **63**, 1191, (1893); for carbon tetrachloride, see Young: *Ibid.* **59**, 932, (1891); for benzene, same: *Ibid.* **55**, 504, (1889); **59**, 134, (1891); for chlorbenzene, same: *Ibid.* **59**, 134; for acetic acid, see Ramsay and Young: *Ibid.* **49**, 790, (1886); Young: *Ibid*, **59**, 909, (1891).

[2] See J. Chem. Soc., **63**, 833, (1893).

the experiment, and σ = density of the vapor at the same temperature.

On the other hand, the results obtained with methyl alcohol, ethyl alcohol, and acetic acid, do not agree with the formula: K is not a constant but varies between comparatively wide limits. In order that K may be a constant with a value between 2.04 and 2.22—as was found in the case of the liquids obeying the law—it must be assumed that the value of $\gamma(Mv)^{\frac{1}{3}}$ does not vary regularly with the temperature. Since γ and v are determined in each case by experiment, the conclusion is drawn that M, in these cases, varies according to the temperature, or, in other words, the molecules of these three liquids are more complex at low than at high temperatures. The relative degree of complexity was calculated as follows: Assuming that the molecular weights of the "non-associating" liquids are the same as their molecular weights in the gaseous state, then we must multiply the "gaseous" molecular weights of "associating" liquids by some factor x to obtain the relative weights of their liquid molecules; x will, of course, vary with the temperature. For acetic acid, then, the equation would become $\gamma(xMv)^{\frac{1}{3}} = K(\tau - d)$, M being taken as 60. Assuming for K the value 2.12, the average of the values found for the six non-asssociating liquids, and using k to denote the value found for the "constant" at any given temperature, the value of x for that temperature was found from the equation $x^{\frac{1}{3}} = \frac{K}{k}$. Thus, at 20° the values of x for acetic acid, methyl alcohol, and ethyl alcohol were found, respectively, to be 3.73, 3.43, and 2.79. As will be shown later, this method of calculating x is not quite correct and gives too high values.

There are many facts known which go to show that the molecular weights of certain liquids vary with change of temperature. Thus Beckmann[1] showed by freezing-point determinations that acetic acid and ethyl alcohol possess more complex molecules in concentrated solution than in the vapor state, whereas the molecular weight of naphthalene does not increase under similar conditions. Cundall[2] has shown that solutions of nitrogen peroxide behave in such a way as to show that the molecules of the oxide are more complex in solution, than in the gaseous state, at the same temperature and

[1] Ztschr. phys. Chem., **2**, 728, (1888) Parizek and Sule conclude from their experiments [Ber. d. chem. Ges., **26**, 1408, (1893)] that water, ethyl alcohol, and the acids of the formic-acid series associate at low temperatures, but that the ethereal salts do not.

[2] J. Chem. Soc., **59**, 1076, (1891).

pressure. Ramsay and Young[1] have also shown that the density of acetic-acid vapor rises as the boiling-point is approached. But for a thorough treatment of this question the reader is referred to the papers of Guye[2] and of Ramsay[3]; the main features of these may be stated in a few words as follows:

(1) Guye has shown[4] that the critical coefficient—*i. e.*, the quotient obtained by dividing the absolute critical temperature by the critical pressure—is equal to the molecular refraction multiplied by a constant with a value of about 1.8. While for most liquids this law holds, the constant for water, methyl alcohol and acetic acid has a value about 1.1, indicating association.

(2) Young and Thomas have shown[5] that the densities of liquids at their critical points may be found by multiplying their theoretical densities by the constant 3.85. The constants in the cases of methyl alcohol, ethyl alcohol, propyl alcohol, and acetic acid are found, however, to be 4.52, 4.02, 4.02, and 5.00, respectively—indicating association.

(3) Young and Thomas have also shown that the method suggested by Cailletet and Matthias for finding the true volume of a liquid at its critical point, while applicable to most llquids, leads to anomalous results in the cases of water, methyl, ethyl, and propyl alcohols, and acetic acid. An explanation of these results is readily found if we assume association for all five substances when in the liquid state, and for the last, acetic acid, in the state of vapor also.

(4.) The heat of vaporization of a liquid diminishes regularly with rise of temperature until the critical temperature is reached, when its value is zero. The total heat absorbed may, however, in the case of a liquid which dissociates with rise of temperature, rise to a maximum and then decrease, owing to the conversion of more complex into simpler molecules. This is found by Ramsay and Young to be the case with ethyl alcohol and acetic acid.

(5.) The vapor-pressure curves of non-dissociating liquids do not cut one another at any point in their course, whereas the curves of dissociating liquids often cut those of normal liquids and at times those of other dissociating liquids. From these curves, then, the fact of the existence of complex molecules in a liquid can be proved.

[1] Phil. Mag., **24**, 196, (1887).
[2] Arch. Sci. phys. nat. Gen., [3], **31**, 38, 164.
[3] Proc. Roy. Soc., **56**, 171, (1894); Ztschr. phys. Chem., **15**, 106.
[4] Ann. chim. phys. [6] **21**, 206, 211; Arch. Sci. phys. nat. Gen., [3], **23**, 197.
[5] J. Chem. Soc., **63**, 1251, (1893); also Phil. Mag., **34**, 507, (1892).

(6.) In van der Waal's vapor-pressure equation

$$\log pc - \log p = f\frac{Tc-T}{T},$$

—where pc and Tc are the critical pressure and temperature, respectively, and p some other pressure to a temperature T,—the constant f has a value closely approximating 3 for all normal liquids. From Young's data for some sixteen liquids the average value is 3.06. Yet for associating liquids f is not constant and its value is higher. Thus its range is 3.56–3.77 for methyl alcohol, 3.58–4.02 for ethyl alcohol, 3.49–3.77 for propyl alcohol, 3.36–3.49 for acetic acid, and 3.20—3.24 for water.

(7.) The ratios of the volumes of saturated vapor at some chosen pressure to that at the critical pressure, as shown by Young,[1] points to association in the case of the acids and the alcohols.

(8.) The same fact is indicated by the greater values, in the case of water and the alcohols, of the heat of vaporization for unit increase of volume.[2]

(9.) Again, in the case of the alcohols, acetic acid, and water, the ratios of total to external work produced on evaporation are higher, showing greater internal work due to dissociation.

Having therefore shown that the connection between surface-energy and molecular weight exists as indicated in the formula $\gamma(Mv)^{\frac{1}{3}} = K(\tau - d)$ through at least a long range of temperature, Ramsay and Shields[3] have made determinations of the surface-energies of a large number of liquids at a comparatively small number of points. The rate of change of the surface-energy with temperature could in this way be found with comparatively little labor. The apparatus was somewhat simplified; the density of the liquid was determined in a jacket of the same vapor as that used for heating the tube containing the capillary; as the temperatures of experiment were low the density of the vapor of the liquid (σ) was omitted in the equation $\gamma = \frac{1}{2}rhg(\rho - \sigma)$. It was found on comparing the data found for certain liquids by the original and by the simplified method that the error of experiment might be as much as 5 per cent.

The following liquids were found to give normal values for K and hence do not associate: Carbon bisulphide, nitrogen

[1] J. Chem. Soc., **63**, 1257 (1893).
[2] See Ramsay and Young: Proc. Phys. Soc., **7**, 303 (1885).
[3] J. Chem. Soc., **63**, 1089 (1893).

peroxide,[1] silicon tetachloride, phosphorus trichloride, phosphorus oxychloride, sulphur dichloride (S_2Cl_2), thionyl chloride ($SOCl_2$), sulphuryl chloride (SO_2Cl_2), nickel tetracarbonyl, normal octane, carbon tetrachloride, ethyl iodide, ethyl mercaptan, ethyl ether, chloral, paraldehyde, methyl formate, ethyl chlorformate, ethyl acetate, acetacetic ether, acetyl chloride, acetic anhydride, ethyl sulphocyanate, ethyl mustard-oil, allyl mustard-oil, benzene, chlorbenzene, benzaldehyde, nitrobenzene, aniline, phenyl cyanide, guaiacol, pyridine, piperidine, quinoline, and methylpropyl ketone.

The following substances have higher molecular weight in the liquid than in the gaseous state: Methyl, ethyl, propyl, isopropyl, butyl, isobutyl, amyl and allyl alcohols; glycol; formic, acetic, propionic, butyric, isobutyric, valeric, and isocaproic acids; acetone; ethyl cyanide, nitroethane; water, and phenol.[2]

The writers find that it is possible, from the data found, to calculate with comparative accuracy the critical temperatures of the liquids examined.

Later determinations by Ramsay and Emily Aston[3] have added to the list of associating substances, bromine, nitric and sulphuric acids. Liquid phosphorus seems to consist of molecules of the formula P_4. It is of interest to note that a constant and very high molecular weight is found for sulphuric acid between 10° and 132°; it then falls rapidly with rise of temperature. The authors call attention, in this connection, to the facts that complex sulphates, such as $NaK_3(SO_4)_2$, are well known, and that the acid has practically no vapor-pressure at ordinary temperatures.[4] The true boiling-point, they therefore conclude, is very much higher than 360°, which is only the point of dissociation under atmospheric pressure.

In order still further to test the accuracy of the formula and the constancy of the value of K for normal liquids, the original method was applied in the determination of the surface-energies of eight more etheral salts, certain necessary data for which had been recently published by Young.[5] The salts used were ethyl formate, methyl acetate, propyl formate, methyl propionate, propyl acetate, ethyl propionate, methyl butyrate, and methyl isobutyrate, and the specimens employed were those originally used by Young. Determinations of surface-

[1] Of course nitrogen peroxide is known to associate in the gaseous state.

[2] For data for phenol, see J. Chem. Soc., **65**, 168 (1894).

[3] *Ibid*, 167.

[4] Johnson [Chem. News, **68**, 211 (1893)] found that no sulphate is formed on leaving caustic soda in a desiccator over sulphuric acid for a month, nor was the liquid alloy of potassium and sodium affected under the same conditions; whereas gold-leaf left for the same period over mercury was heavily amalgamated.

[5] J. Chem. Soc., **63**, 1191 (1893).

tension[1] were made at seven or eight points ranging from 10° to 210°–240°. The value of K ranged from 2.042 for methyl formate, to 2.248 for methyl isobutyrate, increasing with the complexity of the acid radicle.

It seems, therefore, to be established that within wide limits of temperature, the molecular surface-energy of non-associating compounds is a linear function of the temperature. Fourteen such substances have been examined at temperatures ranging from, in certain cases, —89.8° to within a few degrees of the critical temperature, while thirty others have been shown to accord with the law within more restricted limits of temperature. The question now rises, is it fair to assume that for normal liquids the molecular weight in the liquid and gaseous states is the same? When Ramsay and Shields assumed in their earlier work that it was, there was no positive evidence in favor of such a view; there was just as much reason for assuming that the liquid molecules are formed by the union of two, three, or more, gaseous molecules, so far as any experimental data bearing on the question are concerned. Nor was there any physical connection manifest between the equations for the volume-energy of gases and the surface-energy of liquids; their similarity was a mere coincidence. Within the past year, however, van der Waals has published a paper[2] on the thermodynamic theory of capillarity, in which is given a formula for calculating γ, based on purely theoretical grounds, by the application of which the value of γ for ether at —89.8° is found,[3] on calculation, to be identical with the (hitherto unpublished) value found by Ramsay and Shields.

But on other grounds there is much to be said in favor of the assumption. One thing is certain: If, in the case of normal liquids, gaseous molecules unite with one another to form liquid molecules, they all associate to an equal extent, and the degree of association is not altered by rise of temperature. These two assertions are probably not true: it is unlikely that mere liquifaction should produce, in all cases, equal association; and it is unlikely that a rise of temperature should not cause the dissociation of an associated body. Change from the gaseous to the liquid state may be regarded as essentially equivalent to increase of pressure, since each produces approach between the molecules, diminishing intermolecular distance, and bringing so-called molecular forces into play. Now it is well known that equal rise of pressure does not

[1] Proc. Roy. Soc., **56**, 162 (1894); Ztschr. phys. Chem., **15**, 98.
[2] Ztschr. phys. Chem., **13**, 657 (1894).
[3] Proc. Roy. Soc., **56**, 181 (1894); Ztschr. phys. Chem., **15**, 115.

always produce equal increment of association; hence it is unlikely that association to an equal extent should be caused by the reduction of the volumes of compounds until they are approximately equal.[1]

In determining the average molecular weights in the case of associating liquids, it was assumed that there would be a distribution of the simpler and more complex molecules over the capillary surface proportional to the relative quantities of these molecules in the body of the liquid. This assumption has been tested[2] and, in so far as it affects the rate of change of surface-energy, has been found to be justified. Experiments were made with mixtures of (*a*) toluene and piperidine (5 : 1; 1 : 5), (*b*) benzene and carbon-tetrachloride (1 : 1; 10 : 17; 2 : 1), (*c*) chlor-benzene and ethylene bromide (1 : 1), and (*d*) chloroform and carbon bisulphide (1 : 1). The results show that, at least in certain cases, the molecular surface-energy of a mixture is the mean of those of its constituents determined at the same temperature. Further experiments in this direction are now in progress.

Returning[3] finally to the matter of determining the actual molecular weights of associating liquids, Ramsay has pointed out an error in the former work, due to the assumption that the value of x could be determined without taking into account the variation of $x^{\frac{2}{3}}$ with the temperature. More careful examination has shown, however, that this factor must be taken into account. As a result of this examination a formula was deduced which agrees with the results found and avoids the error referred to. The value of x has been thus recalculated for the following liquids:

	Temperature-range.	Range of x.
Methyl alcohol	—89.8°–220°	2.65 –1.75
Ethyl alcohol	—89.8°–230°	2.03 –1.00
Water.....	0°–140°	1.707–1.289
Acetic acid	20°–280°	2.13 –1.30

A recent paper[4] by Guye gives the results obtained by applying still another method to the determination of the molecular weights of liquid hydrocarbons. Making use of the data given by Landolt and Jahn,[5] and by Altschul,[6] he calculates the ratio between the molecular refraction and the critical co-

1 Proc. Roy. Soc., **56**, 166-7 (1894); Ztschr. phys. Chem., **15**, 103.
2 Proc. Roy. Soc., **56**, 182; Ztschr. phys. Chem., **15**, 89.
3 Proc. Roy. Soc., **56**, 175; Ztschr. phys. Chem., **15**, 111.
4 Bull. Soc. chim., (Paris), [3], **13**, 34, (1895).
5 Ztschr. phys. Chem., **10**, 289, (1892).
6 *Ibid.* **11**, 577, (1893).

efficient, and so determines[1] the molecular weight at the critical point. Since, following Ramsay's reasoning, it is more likely that the molecular weights in the liquid and gaseous states are identical than that the substances examined should all associate on liquefaction to just the same extent, he decides that the molecular weight in the gaseous state and that at the critical point are identical. The liquids examined were: pentane, hexane, octane, decane, benzene, toluene, ethylbenzene, the three xylenes, propylbenzene, isopropylbenzene, mesitylene, pseudocumene, isobutylbenzene, and cymene.

The identity of the molecular weights at the critical point and in the gaseous state, is also proved by a comparison of the critical coefficient found for any given substance, and that calculated from the atomic coefficients of the elements which compose it. K_c calculated ranges from 13.8 to 22.8; K_c found, from 13.6 to 21.5, for the substances named, "double-bonds" being supposed absent in the aromatic ring. Assuming the presence of double bonds, the figures found do not coincide so well.

Applying now the method of van der Waals,[2] the identity of the molecular weights of these hydrocarbons in the *liquid* state and at the critical point was demonstrated.

WYATT W. RANDALL.

OBITUARY NOTICES.

JAMES D. DANA.

Though Professor Dana was not a chemist, there are special reasons for noticing his death in this place. The first of these is his position among the scientific men of this country. His untiring devotion to science in the highest sense has served as an inspiration to many who were not working in the same fields, and the effect will continue to be felt. Again, the fact that, notwithstanding his great age, he never gave up work, is one that should be taken to heart by younger men in the hours and days when the sense of weariness comes upon them.

Up to the year 1878 the present writer had sent his chemical articles to the "American Journal of Science and Arts," and they had been kindly received. In the year named, however, a number of articles were sent in together and, in the course of a few days, they were returned with a long and extremely

[1] See §(1), p. 465. [2] See §(6), p. 466.

friendly letter from Professor Dana, in which he made it clear that he could not publish the articles without entirely changing the character of his journal; and, at the same time, he strongly urged the starting of a chemical journal. The letter led to correspondence which resulted in the foundation of this Journal, the first number of which appeared in April, 1879. The editor of the new journal was entirely inexperienced in the work that devolved upon him, and he owes much to the wise counsel and friendly coöperation of Professor Dana.

I. R.

LOTHAR MEYER.

By the death of Lothar Meyer, chemistry loses one of her most philosophical disciples, one whose writings have helped the cause of clear thinking probably as much as those of any other chemist of the last twenty-five years.

Lothar Meyer was born August 19, 1830, at Varel in Oldenburg. He first studied medicine and for a time carried on work in physiology. In 1858 he established himself as *Privatdocent* in the University of Breslau, and became, later, Director of the chemical laboratory. In 1866 he was appointed Professor of Natural Science in the Forestry Academy, at Neustadt-Eberswalde, near Berlin. In 1868 he accepted a call, as Professor of chemistry, to the Polytechnic Institute, at Carlsruhe, and in 1876 he went to Tübingen, where he filled the professorship of chemistry until his death, which occurred April 22.

Meyer was one of the first chemists in Germany to appreciate the full significance of Avogadro's hypothesis. In a note to his edition of Cannizzaro's "Abriss eines Lehrganges der Theoretischen Chemie,"[1] there is an exceedingly interesting account of an attempt made in 1860, by some of the leading chemists, to bring order out of the chaos of chemical thought then prevailing. Meyer was present at the celebrated Carlsruhe convention, and was much impressed by the speech of Cannizzaro. He confesses that "the scales fell from his eyes, and his doubts disappeared, and a feeling of quiet certainty took its place." This experience led him, a few years later, to prepare his well-known "Die Modernen Theorien der Chemie," which appeared in 1864. It was not especially well received at first, but as years passed it exerted a more and more powerful influence on the thoughts of chemists. From a flimsy pamphlet it grew to a stately volume, and it has generally been recognized as the best presentation of the fundamental principles of chemistry until the physicochemical movement began.

[1] Ostwald's Classiker der exakten Wissenschaften. No. 30. Engelmann, Leipzig.

Meyer's name will always be remembered in connection with the Periodic Law. The evidence seems to be conclusive that he recognized the law independently of Mendeléeff and at the same time; and he has since done much to bring out clearly the remarkable relations which exist between the atomic weights of the elements.

As indicated at the beginning of this notice, it was as a chemical philosopher rather than as an experimental investigator, that Meyer gained eminence, though some of his experimental work is of high order. I. R.

GERHARD KRÜSS.

Gerhard Krüss, Ausserordentlicher Professor of Chemistry in the University of Munich, and founder and Editor of the "Zeitschrift für anorganische Chemie," died in Munich, Feb. 3, aged 36. Krüss began the study of chemistry in 1879 at Munich, and, excepting a summer with Bunsen in Heidelberg and a winter with Nilson in Stockholm, he remained in Munich as student, assistant, privatdocent, and professor until his death. Krüss was a rapid and accurate worker, and a man of unflagging industry and energy. Between 1882 and the present year, he published sixty-nine articles embodying the results of his own work, and that of his pupils. Among his more important investigations are those on the sulphur derivatives of molybdenum, on the atomic weight of gold, on the double sulphocyanates of iron, on the vanadium sulphides of chromium, on beryllium, on various rare earths. Krüss was a skillful spectroscopist. In 1891 he published with his brother, Hugo Krüss, a book entitled "Colorimetry and Quantitative Spectrum Analysis," which is of high value and was favorably received. In 1892 he published his manual of "Special Analytic Methods," a second edition of which was printed in the following year. Krüss wrote the articles on inorganic chemistry in Richard Meyer's "Jahrbuch der Chemie," in the years 1892, 1893, 1894. In 1892 Krüss founded the "Zeitschrift für anorganische Chemie." The science of inorganic chemistry loses in Gerhard Krüss an indefatigable worker, and a teacher who knew how to inspire his pupils with his own enthusiasm. E. R.